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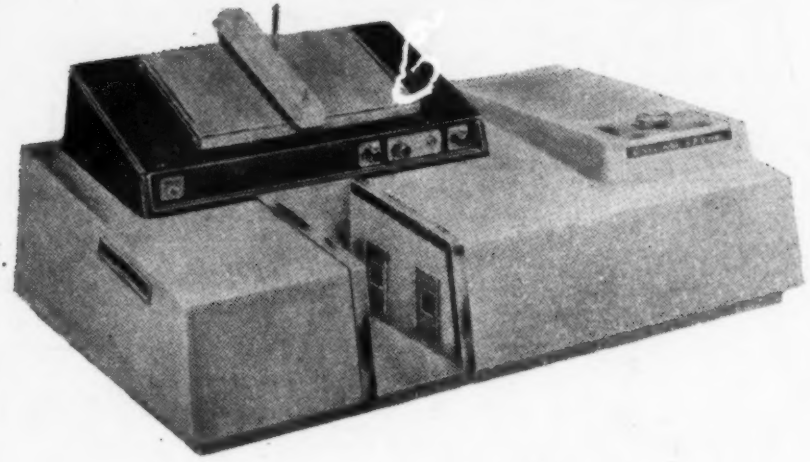

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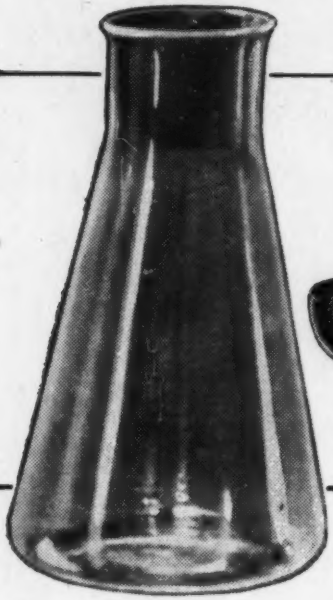

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JOURNAL OF THE INDIAN CHEMICAL SOCIETY

JANUARY, 1961

## Contents

Page

1. Organic derivatives of boron. Part I. Synthesis by alcohol interchange technique.—By R. C. Mehrotra and G. Srivastava .. .. .. 1

2. Reduction of cobalt borate by hydrogen.—By Miss Rowshan Jahan and M. H. Khundkar .. .. .. .. .. 7

3. Light scattering behaviour of thorium phosphate gel-forming system.—By U. M. Purao and D. M. Desai .. .. .. .. .. 11

4. β-Phenylethanol amines. Part II. Studies on cyclodehydration of a few acylamino alcohols.—By N. Adityachaudhury, S. K. Srimany, and (Mrs.) A. Chatterjee .. .. .. .. .. 15

5. A study on complex formation of beryllium with salicylic and sulphosalicylic acids.—By Rebati Charan Das and S. Aditya .. .. .. 19

6. Studies on 2-*o*-anisylimino-3-*o*-anisyl-4-thiazolidone, 3-*o*-anisyl-2,4-thiazolidione, 2-*o*-phenetylimino-3-*o*-phenetyl-4-thiazolidone, 3-*o*-phenetyl-2,4-thiazolidione, and the fungicidal activity of the acetoxymercuri derivatives of the thiazolidiones.—By P. N. Bhargava, Miss Kamalini Bhargava, and R. C. Kapoor .. .. .. .. .. 23

7. Studies in the synthesis of biphenyls.—By C. S. Kallianpur and J. R. Merchant .. 27

8. Substituted phenylhydrazines and their derivatives.—By Shiam Sunder Joshi and Daleep Singh Deorha .. .. .. .. .. 31

9. Ultraviolet absorption spectra of sulphones. Part IV. Effect of *ortho*-substituents.—By V. Baliah and T. Rangarajan .. .. .. 33

10. Behaviour of chloronitrobenzenes with hydrazine and hydrazine derivatives. Part XII. 2-Phenyl-1,2,3-benzotriazoles and their 1-oxides.—By Daleep Singh Deorha and Shiam Sunder Joshi .. .. .. 41

11. 1-Alkyl-substituted 2,4-dithiobiurets and related thiurets: Interaction of aliphatic amines and isopersulphocyanic acid.—By S. N. Dixit .. 44

12. Charge and stability of colloids. Part XXIII. Displacement of hydrogen ions from $Sb_2S_3$ sol by addition of electrolytes in presence and in absence of non-electrolytes.—By B. P. Yadava and Mohammad Yaseen .. 47

13. Studies on the Fries rearrangement. Part II.—By S. S. Tiwari and A. Singh .. 53

Short Notes :

1. Effect of alkali on the reduction of potassium permanganate by selenium dioxide.—By Kundan Lal and Mohinder Singh Sohal .. .. 57

2. Synthesis of nitrophenacyl bromides.—By H. G. Garg .. .. 59

## FOR AUTHORS ONLY

*Extracts from the "Style Guide for Chemists" by Fieser & Fieser will be published henceforth in each issue of this Journal so that authors may take advantage in improving the quality of their composition and presentation.

### 1.1. Avoid needless words.

A word that contributes nothing to the meaning should always be omitted (see the words below in parantheses).

(Thus) a substance that dissolves easily in ligroin is usually insoluble in water.
Obviously (, then,) the sharpness of the melting point.....
An impure sample may (, of course,) be a mixture of individually pure compounds.
(Now) the analyses show that .....
The results (which were) obtained .....

### 1.2. Some laboratory colloquialisms violate rule 1.1.

Each of the following familiar expressions contains an unnecessary word that adds little or nothing to the meaning and hence is technically incorrect in formal writing.

Heating is continued as long as the alcohol distills (over).
.....crystallizes (out).....precipitates (out).
The material is pressed (down) well with a spatula.
.....to evaporate (off) the ether.
Wash (out) the flask with water.
The funnel is rinsed (out) with a little ether.
.....fraction boiling (up) to 150°.

### 1.3. Avoid the impersonal "it".

"It is interesting to note that....." is weak and pompous. Such an indirect expression is useless, and consequently should be omitted; in other cases it can be replaced by a simpler expression :

It will be seen that.....(omit)
It is evident that.....(Evidently.....)
It would appear that.....(Apparently.....)
It is then clear that.....(Clearly.....)
It would thus seem that (Seemingly.....)
It is of interest that.....(Interestingly.....)
It is our conclusion that.....(We conclude that.....)

### 1.4. Avoid overuse of "the".

The definite article can be omitted from each of the following expressions without change in meaning :

.....to attempt *the* synthesis of compounds.....
.....a method for *the* introduction of oxygen at $C_{11}$.....
.....can be employed satisfactorily for *the* technical production.....

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# Organic Derivatives of Boron. Part I. Synthesis by Alcohol Interchange Technique

**R. C. Mehrotra and G. Srivastava**

The reactions of ethyl borate with butanols (*n* & *tert.*), ethylene glycol, catechol, salicylic acid, and anthranilic acid have been studied in different stoichiometric ratios in refluxing benzene. The alcohol produced has been removed azeotropically with benzene; the advantages of this technique have been discussed.

The following compounds have been synthesised by the above procedure: ethyl dibutyl$^t$borate, ethyl ethyleneborate, diethylene ethylenedi-(borate), ethyl and butyl$^t$ *o*-phenyleneborates, tri-*o*-phenylene-bis-borate, borosalicylic acid, ethoxyboron anthranilate.

Alcohol interchange technique has been extensively employed by one of the authors and also others for the preparation of derivatives of aluminium (Mehrotra, this *Journal*, 1953, **30**, 585; 1954, **31**, 85), titanium (Bradley, Mehrotra, and Wardlaw, *J. Chem. Soc.*, 1952, 2027, 4204), zirconium (Mehrotra, this *Journal*, 1954, **31**, 904; Bradley and Wardlaw, *J. Chem. Soc.*, 1951, 280), niobium (Bradley *et al.*, *ibid.*, 1958, 99), and uranium (Bradley *et al.*, *Proc. Chem. Soc.*, 1957, 260). The advantages of the azeotropic distillation of ethanol or isopropanol, produced in reactions of this type, have been emphasised in a recent publication (Mehrotra, *loc. cit.*).

In spite of very active interest in the field of similar derivatives of boron, the technique of alcohol interchange has been employed to a very limited extent. This technique was first employed in the case of boron by Wuyts and Duquesne (*Bull. Soc. Chem. Belg.*, 1939, **48**, 77) to prepare organo-boron compounds. Several compounds were prepared by them by distilling a mixture of the alcohol or phenol with a 25% excess of propyl$^n$ borate. Propanol formed during the reaction was removed by distillation at atmospheric pressure and the excess of propyl borate was distilled off at a reduced pressure.

Thomas (*J. Chem. Soc.*, 1946, 820, 823) also applied the same technique, taking a slight excess of alcohol or phenol in place of borate, to preparation of those compounds, which could not be prepared from boric acid or oxide and alcohol.

Thus the azeotropic distillation technique of alcohol interchange does not appear to have been used in the case of boron at all. Apart from the advantage of employing only a slight excess of the alcohols or other reagents and removing the ethanol produced azeotropically with benzene, the technique has the unique advantage that reactions in required stoichiometric proportions can be carried out with its help. Thus an attempt has been made to prepare mixed alkoxides of boron by the following simple reactions:

$$B(OEt)_3 + BuOH + \text{benzene} \rightarrow (OBu)\,B\,(OEt)_2 + \underbrace{EtOH + \text{benzene}}$$

$$B(OEt)_3 + 2BuOH + \text{benzene} \rightarrow (OBu)_2\,B\,(OEt) + \underbrace{2EtOH + \text{benzene}}$$

Although stable mixed derivatives could not be prepared in the case of acyclic alcohols (*n*- and *tert.*-butanols), the technique has readily furnished stable mixed compounds with glycol and catechol. Further syntheses of salicylate and anthranilate derivatives have been attempted by the new technique.

(*a*) *Normal Alkoxides.*—The reaction between ethyl borate and butanol$^n$ is very fast and tributyl borate can be quantitatively prepared from ethyl borate by taking almost the theoretical quantity of the alcohol.

$$B(OEt)_3 + 3\ BuOH \rightarrow B(OBu)_3 + 3\ EtOH \uparrow$$

When the reaction is carried out in 1 : 2 molar ratio with a view to preparing the mixed borate $B(OEt)(OBu^n)_2$, two moles of ethanol are, however, removed azeotropically, as found by analysis, indicating that the reaction :

$$B(OEt)_3 + 2\ BuOH \rightarrow (OEt)\ B\ (OBu)_2 + 2\ EtOH \uparrow$$

(I)

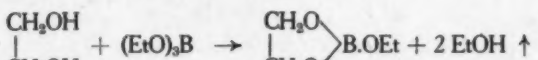
has gone to completion. Compound (I) on distillation, however, undergoes disproportionation, affording a mixture of $B(OEt)_3$, $B(OEt)_2(OBu)$, $B(OEt)(OBu)_2$, and $B(OBu)_3$.

Previously Schiff (*Annalen Suppl.*, 1867, **5**, 183) had claimed to have prepared such compounds by heating two tri-alkyl borates together. Later, similar experiments were carried out by Thomas (*loc. cit.*) by refluxing a mixture of two alcohols (3 g. moles of each), boric anhydride, and benzene and allowing the condensed vapours to percolate through anhydrous copper sulphate to remove the water formed during the reaction, and distilling the mixed borate formed under reduced pressure. He showed that such acyclic mixed borates disproportionated readily on distillation and observed that Schiff's claim rested on fortuitous analyses of the appropriate distillation cuts.

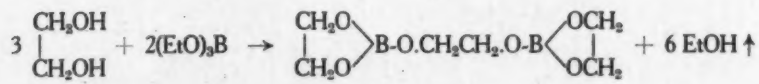
(*b*) *Tertiary Alkoxides.*—The reaction of ethyl borate with butanol$^t$ is comparatively very slow and almost stops after the replacement of two moles of ethoxy group, thus affording the mixed borate $B(OC_2H_5)(OC_4H_9^t)_2$ (II).

The actual formation of (II) in solution is supported by the extremely slow nature of the reaction after two moles of ethanol have been distilled. Similar observations have been made in the case of aluminium ethoxide- butanol$^t$ interchange (Mehrotra, *loc. cit.*) and these have been ascribed to steric hindrance to the replacement of the third alkoxy group. This compound also disproportionates, however, on distillation although the rate of disproportionation is slow as even the last fraction after double distillation of the compound is not a pure sample of butyl$^t$ borate.

(*c*) *Glycolates.*—The reaction between ethyl borate and ethylene glycol in equimolar ratio gives rise to a compound with replacement of two moles of ethoxy group, corresponding to the formation of ethyl ethyleneborate (III). When the reaction is carried out in 2 : 3 molar ratio, diethylene ethylenedi-(borate) (IV) is formed.



(III)

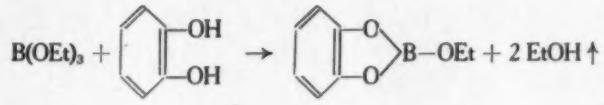


(IV)

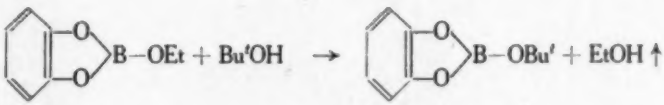
The above two compounds have been previously prepared by Blau *et al.* (*J. Chem. Soc.*, 1957, 4116) ; compound (III) by the action of ethanol on ethylene chloroboronate and (IV) by the interaction of $BCl_3$ and ethylene glycol in 2 : 3 molar ratio. Although these compounds provide

similar analytical data, compound (III) differs in physical properties, the cause of which is under investigation.

(*d*) *Catecholates.*—Reaction between ethyl borate and catechol in equimolar ratio furnishes the compound, ethyl *o*-phenyleneborate (V). The alcoholysis of ethyl *o*-phenyleneborate with butanol$^t$ affords *butyl$^t$ o-phenyleneborate* (VI).

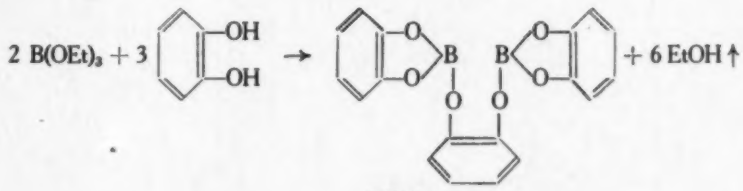


(V)



(VI)

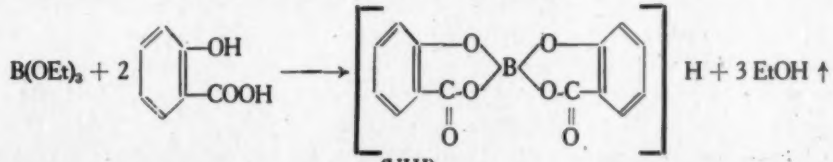
When ethyl borate and catechol are allowed to react in 2 : 3 molar ratio, tri-*o*-phenylene-bisborate (VII) is obtained, which has also been prepared from boric acid and catechol by removing the water formed during the reaction azeotropically with benzene.



(VII)

Previously Gerrard *et al.* (*J. Chem. Soc.*, 1959, 1529) prepared compound (V) by the action of ethanol on *o*-phenylene chloroboronate and compound (VII) by reacting $BCl_3$ and catechol in 2 : 3 molar ratio. Compound (VI) is a new one. The preparation of the new compound (VI) by a simple replacement reaction shows in a pronounced degree the advantage of the new technique, as the reaction of butanol$^t$ with *o*-phenylene chloroboronate will fail in this case to produce compound (VI) due to the side reaction of butanol$^t$ with hydrogen chloride.

(*e*) *Salicylate.*—Ethyl borate reacts with salicylic acid in 1 : 2 molar ratio, giving out all the 3 moles of ethanol with the formation of *borosalicylic acid* (VIII).

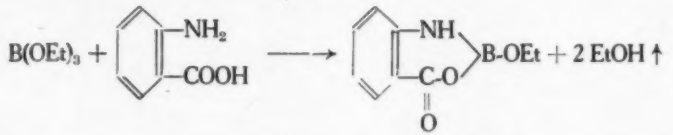


(VIII)

When the reaction is carried out in equimolar ratio, the same compound is formed, half of ethyl borate remaining unchanged.

Foelsing (D.R.P., 230,725 ; 288,388) described the preparation of a zinc salt of borosalicylic acid and the free acid, but Meulenhoff (*Rec. trav. chim.*, 1925, **44,** 150) could not repeat the preparation of either of them though he prepared a number of other salts of borosalicylic acid. Preparation of boron trisalicylate has been reported by Hirao and Yabwichi (*J. Pharm. Soc., Japan*, 1954, **74,** 1073) from boric acid and salicylic acid, and by Ahmad, Haider, and Khundkar (*J. Appl. Chem.*, 1954, **4,** 543) by the action of salicylic acid on boron triacetate, but their work is doubtful in view of the results reported by Gerrard and Mooney (*Chem. & Ind.*, 1958, 227).

(*f*) *Anthranilate.*—Anthranilic acid reacts with ethyl borate in equimolar ratio, furnishing *ethoxyboron anthranilate* (IX) according to the following scheme :



The above is a new type of reaction showing the easy replaceability of ethanol groups simultaneously by an amino and a carboxylic acid group in *ortho* position in the benzene ring. The synthesis and the identity of the compound have been confirmed by repeated analyses and molecular weight measurements in ether. Incidentally, the reaction of benzoic acid with ethyl borate will give rise to ethyl benzoate according to the following scheme (Hirao and Yabwichi, *loc. cit.*) :

$$B(OEt)_3 + 3\ C_6H_5COOH \rightarrow 3\ C_6H_5COOEt + B(OH)_3.$$

The reaction of ethyl borate with aniline was attempted by Jones and Kinney (*J. Amer. Chem. Soc.*, 1939, **61,** 1378), who reported negative results. On refluxing ethyl borate with excess aniline for 10-12 hours, boron tri-anilide (in very low yield) could, however, be synthesised according to the reaction :

$$B(OEt)_3 + 3\ C_6H_5NH_2 \rightarrow B(NHC_6H_5)_3 + 3\ EtOH$$

## EXPERIMENTAL

All-glass apparatus fitted with interchangeable joints was used throughout and special precautions were taken to exclude moisture. Fractionations were carried out in a column (30 inches) packed with Raschig rings and fitted to a total-condensation variable take-off stillhead.

Benzene (B.D.H.,L.R.) was dried over sodium and redistilled. Butyl$^t$ alcohol (B.D.H.,L.R.) was dried over calcium oxide, followed by distillation over sodium butoxide$^t$. Other alcohols were dried by the usual procedures and were finally purified by careful fractionation.

Ethyl borate was prepared from boric oxide and ethanol (Webster and Dennis, *J. Amer. Chem. Soc.*, 1933, **55,** 3233), removing the water formed during the reaction as a ternary azeotrope of water, ethanol, and benzene.

*Analytical Methods.*—Boron was determined by hydrolysing the compound and titrating the boric acid formed with sodium hydroxide in presence of mannitol. In those compounds, which gave acids or bases besides boric acid on hydrolysis, boron was estimated by Thomas' method (*loc. cit.*).

Nitrogen was estimated by Kjeldahl's method. Ethoxide was determined by a back-titration method (Bradley and Wardlaw, *J. Chem. Soc.*, 1950, 3450). The method of estimation is not affected by the presence of butanol$^t$ or butoxide$^t$ group (Mehrotra, *loc. cit.*). Salicylic acid was determined by alkaline permanganate method.

Molecular weights were determined ebullioscopically in benzene and ether by a semi-micro ebulliometer (Gallenkamp) employing thermositor sensing. Concentrations were plotted against $\Delta R$ (decrease in resistance) and a straight line was obtained in each case.

*Reaction between Ethyl Borate and Butanol*$^n$.—To ethyl borate (9.3 g.) in benzene (50 g.) was added butanol$^n$ (16 g.) and the mixture was refluxed at bath temperature of 120-30° for half an hour. The azeotrope coming at 68° was then slowly taken. Ethanol obtained in the azeotrope was 8.75 g. (3 moles require 8.79 g.). The excess of benzene was distilled off at a high reflux ratio. Finally butyl$^n$ borate (13.2 g.) was distilled at 128°. [Found : B, 4.71. Calc. for $B(OC_4H_9)_3$ : B, 4.7%].

Ethyl borate (12.61 g., 1 mole) in benzene (40 g.) and butanol$^n$ (12.8 g., 2 moles) were refluxed for half an hour at bath temperature of 120-30°. The azeotrope coming at 68° was then slowly taken. Ethanol obtained in the azeotrope was 7.8 g. (2 moles require 7.95 g.). Excess of benzene was removed and the compound was distilled at 25 mm pressure. First fraction (5 g., B 7%) distilled between 60° and 85° and the second fraction (12.5 g., B 5.1%) distilled between 85° and 97°. [Calc. for $B(OEt)_3$ : B, 7.4% and for $B(OBu)_3$ : B, 4.7%].

*Reaction between Ethyl Borate and Butanol*$^t$.—To ethyl borate (10.83 g.) excess of butanol$^t$ and benzene were added five to six times and each time the mixture was refluxed for 4-5 hours. The temperature of the distillate was about 68° in the beginning, but rose to nearly 70° after a few drops were taken out. For the rest of the reaction the distillate, consisting of azeotropic mixtures of ethyl and butyl$^t$ alcohols and benzene, was slowly collected between 70° and 71° and ethanol was determined in it every time. After 6.8 g. (2 moles require 6.82 g.) of ethanol had been removed, the reaction almost stopped as the temperature of the distilling liquid did not show any tendency of lowering below 73° (b.p. of benzene-butanol$^t$ azeotrope) and this was confirmed by lack of reducing power (tested with $K_2Cr_2O_7$) of the distillate. Excess of benzene and butanol$^t$ was distilled off and the compound was distilled at 20 mm pressure. First fraction (3 g.) distilled up to 40°, smelt like benzene, and it was rejected. Second fraction (2.5 g., OEt 15.5%) was obtained between 40° and 60° and the third fraction (7 g., OEt 10.1%) was obtained between 60° and 75°. Third fraction was redistilled. [Found : OEt, 8.8 ; B, 4.9. Calc. for $B(OBu)_3$ : B, 4.7%].

*Reaction between Ethyl Borate and Ethylene Glycol.*—Ethyl borate (11.76 g., 1 mole) in benzene (50 g.) was refluxed with glycol (4.99 g., 1 mole) for an hour at bath temperature of 120-30°. The azeotrope coming at 68° was then slowly taken. Ethanol obtained in the azeotrope was 7.3 g. (2 moles require 7.41 g.). Excess of benzene was removed at 30°/5 mm. A colorless semisolid (9.4 g.) was obtained. (Found : B, 9.3. Calc. for $C_4H_9O_3B$ : B, 9.3%).

Ethyl borate (12.18 g. 2 moles) in benzene (50 g.) was refluxed with glycol (7.76 g. 3 moles) for 2 hours at bath temperature of 120-30°. The azeotrope coming at 68° was then slowly taken ; 10.51 g. of ethanol (6 moles require 11.5 g.) was obtained in the azeotrope. On removing the excess of benzene at 30°/5 mm, a white powder (8.4 g., m.p. 160-62°) was obtained. [Found : B, 10.6. Calc. for $B_2(O_2C_2H_4)_3$ : B, 10.7%].

*Reaction between Ethyl Borate and Catechol.*—Ethyl borate (7.76 g., 1 mole) in benzene (40 g.) was refluxed with catechol (5.85 g., 1 mole) for 2 hours and the azeotrope coming at 68° was then slowly taken ; ethanol obtained was 4.69 g. (2 moles require 4.89 g.) in the azeotrope. Excess of benzene was distilled off when ethyl *o*-phenyleneborate was obtained as a colorless liquid (6.63 g.), distilling at 86°/8 mm, 0.86 g. remaining undistilled. (Found : B, 6.45. Calc. for $C_6H_4O_2BOEt$ : B, 6.6%).

Ethyl *o*-phenyleneborate (3.1 g.) in benzene (35 g.) was refluxed with butanol$^t$ (4 g.) for 2 hours; the azeotrope coming at 68° was taken slowly; 0.82 g. ethanol (1 mole requires 0.97 g.) was obtained. After removing the excess of benzene, butyl$^t$ *o*-phenyleneborate was obtained as a colorless liquid (3.6 g., 90%), distilling at 85-87°/3 mm. (Found : B, 5.5; M.W., 197. $C_6H_4O_2$-BOBu requires B, 5.6%; M.W., 192).

Ethyl borate (7.3 g., 2 moles) in benzene (40 g.) was refluxed with catechol (8.25 g., 3 moles) for 3 hours and the azeotrope, taken as usual, gave 6.72 g. ethanol (6 moles require 6.9 g.). Excess of benzene was distilled off and tri-*o*-phenylene-bis-borate (7.5 g.) was distilled at 214°/4 mm., 1 g. residue remaining undistilled. The compound solidified at once. [Found : B, 6.1. Calc. for $B_2(C_6H_4O_2)_3$ : B, 6.3%].

A mixture of boric acid (4.74 g., 2 moles), catechol (12.62 g., 3 moles), and benzene (50 g.) was refluxed for 2 hours and then slowly fractionated. After distilling the azeotrope of water and benzene, excess of benzene was distilled rapidly. Tri-*o*-phenylene-bis-borate was distilled at 214-18°/4 mm. (12.72 g.). [Found : B, 6.15. Calc. for $B_2(C_6H_4O_2)_3$ : B, 6.3%].

*Reaction between Ethyl Borate and Salicylic Acid.*—Ethyl borate (6.20 g., 1 mole) in benzene (40 g.) was refluxed with salicylic acid (11.71 g., 2 moles) for 2 hours and the azeotrope taken at 68° furnished 5.4 g. ethanol (3 moles require 5.85 g.). After distilling the excess of benzene, the compound was dried at 30°/5 mm. After washing it with dry ether, borosalicylic acid was obtained in 10.75 g. yield. It is soluble in acetone and ethyl acetate. [Found : B, 3.53; $C_7H_4O_3$, 96. $B(C_7H_4O_3)_2H$ requires B, 3.8; $C_7H_4O_3$, 95.7%].

Ethyl borate (7.88 g., 1 mole) in benzene (45 g.) was refluxed with salicylic acid (7.43 g., 1 mole) for 2 hours. The azeotrope at 68° gave 3.6 g. ethanol (1.5 moles require 3.72 g.). After removing the excess of benzene, the compound was washed with ether several times and dried at 30°/5 mm. Borosalicylic acid obtained was 7.2 g. [Found : B, 3.57; $C_6H_4O_3$, 96.7. $B(C_7H_4O_3)_2H$ requires B, 3.8; $C_7H_4O_3$, 95.7%].

*Reaction between Ethyl Borate and Anthranilic Acid.*—Ethyl borate (5.32g., 1 mole) in benzene (50 g.) was refluxed with anthranilic acid (4.99 g., 1 mole) for 2 hours. The azeotrope at 68° gave 3.2 g. of ethanol (2 moles require 3.35 g.). The compound was crystallised in benzene. The mother liquor was decanted and the compound was washed with dry benzene. Ethoxyboron anthranilate obtained (6.1 g.) was purified by sublimation at 120-40°/3mm. (Found : B, 5.55. N, 7.01; M. W., 206. $C_9H_{10}O_3NB$ requires B, 5.7; N, 7.33%; M. W., 191).

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# Reduction of Cobalt Borate by Hydrogen

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Reduction of the crystalline cobalt borate, $CoO.3B_2O_3$, by hydrogen proceeds according to

$$CoO.3B_2O_3 + H_2 = Co + 3B_2O_3 + H_2O.$$

The reduction is slow up to 550°, but becomes increasingly rapid with increase of temperature. At 750° reduction is more than 90%, but complete reduction is hindered by fusion of the borate itself. The reduction process, like those for copper and nickel borates, is accompanied by activated adsorption.

The present investigation is a continuation of our previous work in this laboratory on copper and nickel borates (this *Journal*, 1956, **33**, 555; *Indian J. Appl. Chem.*, 1958, **21**, 81). No information is available in the literature on the reducibility of cobalt borate by carbon or hydrogen. Results on the reduction of a cobalt borate is reported in the present communication.

## EXPERIMENTAL

### *Cobalt Borate*

Preparation of cobalt borate by metathesis from aqueous solution was more difficult than the corresponding copper or nickel salt. The light pink precipitate first formed easily changed colour to blue simply on exposure to air, indicating decomposition to basic compounds. Fusion methods were also not entirely satisfactory because of the difficulty of purification and isolation of a borate having a definite composition.

A very interesting but simple method was developed for the preparation of a pure cobalt borate. The starting material was a dihexammino-dicobaltic borate, $[Co(NH_3)_6]_2(B_4O_7)_3.14H_2O$, prepared according to the method of Khundkar and Haider (*Z. anorg. allgem. Chem.*, 1956, **284**, 312). On slowly heating this compound at 450°, the deep yellow crystals decomposed, giving off both ammonia and water vapour, and finally a violet-blue cobalt borate was obtained. This on analysis conformed to the composition $CoO.3B_2O_3$. (Found: B, 22.8, 22.5; Co, 20.2, 21.0. Calc. for $CoO.3B_2O_3$: B, 22.9; Co, 20.8%).

### *Procedure*

The apparatus was the same as that employed for reduction of copper borate (*loc. cit.*). The cobalt borate (previously heated to remove any moisture, and cooled) was taken in a platinum boat and placed in the reaction temperature zone in a closed system, which had earlier been evacuated and filled with pure hydrogen at atmospheric pressure. The progress of the reaction was followed by noting the decrease in gas volume at different intervals of time; these volumes were corrected for N.T.P. and plotted against time in Fig. 1. The water vapour formed during the reaction was absorbed in $P_2O_5$, placed in a small boat at the exit (cooler) end of the reaction tube.

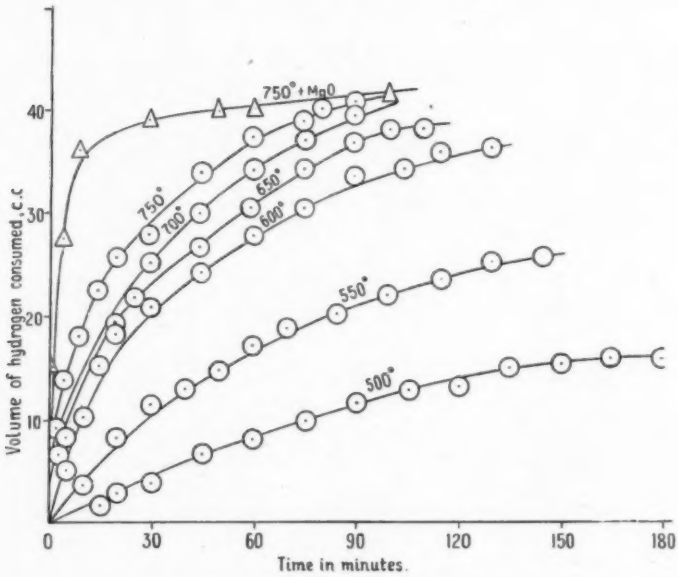
*Analysis of the Products of Reduction.*—The solid products of reduction were free $B_2O_3$, metallic cobalt, and cobalt borate. The amount of free $B_2O_3$ gave the extent of reduction. Great

care was necessary to extract this from unreduced cobalt borate, and it was possible only with anhydrous methanol. Hot water or even hot methanol decomposes cobalt borate (giving methyl borate in the latter case).

## DISCUSSION

For the different experiments carried out at temperatures between 500° and 750°, equal amounts of cobalt borate (0.4 g.) were taken so that the results could be directly compared. Progressive consumption of gas with time (Fig. 1) shows that the reaction is somewhat slow up to 550°, taking nearly 160 to 180 minutes to reach equilibrium. At temperatures between 600° and 750°, the major reaction takes place during the first hour.

FIG. 1




The theoretical amount of hydrogen required for complete reduction to cobalt (without affecting $B_2O_3$) is 31.9 c.c. At 600° and above, the total volume of hydrogen consumed is higher than this. It had earlier been noted that $B_2O_3$ was not reduced at all by hydrogen at these temperatures. It is therefore obvious that the reduction process is associated with adsorption of gas, presumably on the reduced metal.

### *Extent of Reduction at Different Temperatures*

Free $B_2O_3$ was always found in the products of reduction; this could be extracted, without affecting the residual cobalt borate, by cold anhydrous methanol. The mechanism of reduction of cobalt borate appears to follow the general course, as found earlier with copper and nickel borates, viz.,

$$CoO.3B_2O_3 + H_2 = Co + H_2O + 3B_2O_3.$$

The amount of free boric anhydride (as extracted by careful and repeated extraction with anhydrous methanol) was determined in the product of each experiment and expressed in terms of percentage of total $B_2O_3$ (present in $CoO.3B_2O_3$).

TABLE I

*Products of reduction of cobalt borate by hydrogen at diff. temp.*

$CoO.3B_2O_3$ taken = 0.400 g., corresponding to 0.294 g. $B_2O_3$.

| Reduction. Temp. | Period. | $B_2O_3$ in methanol extract. | | $B_2O_3$ in unchanged borate. | | Mean value of reduction. |
|---|---|---|---|---|---|---|
| 500° | 195 min. | 0.096 g. | 32.6 % | 0.192 g. | 65.4 % | 33.6 % |
| 550° | 145 | 0.148 | 50.3 | 0.139 | 47.4 | 51.4 |
| 600° | 130 | 0.198 | 67.4 | 0.094 | 32.0 | 67.7 |
| 650° | 110 | 0.222 | 75.5 | 0.067 | 22.8 | 76.4 |
| 700° | 90 | 0.245 | 83.2 | 0.050 | 17.1 | 83.1 |
| 750° | 90 | 0.266 | 90.4 | 0.028 | 9.6 | 90.4 |

The data in Table I (column 4) could be taken to represent the extent of reduction at the relevant temperature. But this was further corroborated by the determination of total $B_2O_3$ in the unchanged borate (*i.e.*, residue from anhydrous methanol extract), and expressed as percentage (Table I, column 6). The difference between 100 and these values would also represent the extent of reduction ; the mean of the two values was actually taken in the last column.

Instead of continuing for the same period of time, the experiments were continued till the system came to equilibrium, *i.e.*, when the rate of consumption of hydrogen came down to $< 1.0$ c.c. per hour.

The extent of reduction is small at 500° ; this increases with temperature and reaches only 90% at about 750°. A plot of the percentage of reduction against temperature (not shown here) indicates that the slope of the curve between 500° and 600° is greater than that between 600° and 750°. This is explained by the observation that the cobalt borate tends to sinter above 600° and actually fuses between 700° and 750°. This means that complete reduction of cobalt borate by hydrogen is not practically feasible. The reduction, however, proceeded to over 90%.

In an attempt to stop fusion of cobalt borate, two experiments were carried out at 700° and 750° respectively with MgO as incorporate. In presence of MgO, the rate of reaction was very much accelerated (Fig. 1), but the total gas consumption was more or less the same. Whether the reduction went to completion could not be confirmed on account of the meagre amount of free $B_2O_3$ found in methanol extract. This is possible only if MgO reacts (partially or completely) with cobalt borate as follows :

$$CoO.3B_2O_3 + 3MgO = 3MgO.B_2O_3 + CoO.$$

This can also explain the rapidity of reduction in presence of MgO ; CoO is known (cf. Mellor, "Comprehensive Treatise on Inorganic & Theoretical Chemistry", Vol. 14, p. 563) to be very rapidly reduced by hydrogen at 700°.

*Phenomenon of Adsorption*

In Table II is presented a set of data showing (*i*) the volume of hydrogen (N.T.P.) consumed during reaction, as obtained from curves in Fig. 1, (*ii*) the volume of hydrogen required for reduction at different temperatures, as calculated from the extent of reduction, and (*iii*) the difference of the above two, representing the volume of hydrogen adsorbed.

TABLE II

[$CoO.3B_2O_3$ taken in each experiment = 0.400 g.]

| Temp. | Reduction Mean value. | Actual vol. (total) of $H_2$ consumed. | Volume of $H_2$ reqd. for reduction. | Volume of $H_2$ in excess. |
|---|---|---|---|---|
| 500° | 33.6 % | 15.1 c.c. | 10.7 c.c. | +4.4 c.c. |
| 550° | 51.4 | 25.3 | 16.4 | 8.9 |
| 600° | 67.7 | 35.9 | 21.6 | 14.3 |
| 650° | 76.4 | 37.7 | 24.4 | 13.3 |
| 700° | 83.1 | 39.3 | 26.5 | 12.8 |
| 750° | 90.4 | 40.5 | 28.9 | 11.6 |
| 700° (with 0.1 g. MgO) .. | | 38.7 | .. | .. |
| 750° (with 0.1 g. MgO) .. | | 41.2 | .. | .. |

The data in Table II leave no doubt that the system $CoO.3B_2O_3$—$H_2$ also falls in general line with the other systems (viz., involving $CuO.B_2O_3$ and $2NiO.B_2O_3$) so far studied in that this reduction process is also accompanied by adsorption. In all probability the adsorption takes place on the finely divided metal after it has been formed by reduction of the borate. It should be noted that the adsorption is relatively low up to 550°, after which it increases, but the values between 600° and 750° do not differ much. A common factor in all the three systems, mentioned above, is that this adsorption has a positive temperature coefficient (activated adsorption) as noted by Taylor *et al.* for certain oxides (*J. Amer. Chem. Soc.*, 1931, **53**, 2168).

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# Light Scattering Behaviour of Thorium Phosphate Gel-forming System

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The changes in depolarisation values and in intensity of transversely scattered light of thorium phosphate gels, prepared by diluting acid solutions of thorium phosphate, have been investigated. The results show that the particles grow in size owing to agglomeration. This study also reveals that the particles in the set gels are very nearly spherical in shape. The intensity values show a gradual change initially; thereafter it attains a steady value. The dissymmetry: ratio $I_{45}°/I_{135}°$ fails to provide true indication of probable shape of the particles in this system.

Thorium phosphate gels were first prepared by Prakash and Dhar (this *Journal*, 1929, **6,** 587) by mixing thorium nitrate and potassium phosphate solutions in suitable concentrations. The gels obtained were either transparent or translucent. Mehta, Parmar and Prasad (*ibid.*, 1936, **13,** 128) have shown that perfectly transparent gels of thorium phosphate could be obtained by using phosphoric acid, instead of potassium phosphate. They reported that perfectly transparent gels could also be obtained by suitably diluting a saturated solution of thorium phosphate in hydrochloric acid. The optical properties of these gels, prepared by directly mixing solutions of thorium nitrate and potassium phosphate, have been studied in details by Desai and Guruswami (*Proc. Ind. Acad. Sci.*, 1943, **18A,** 31) and by Prasad and Doss (*J. Col. Sci.*, 1949, **4,** 349). The former have studied the effect of HCl and non-electrolytes on the rate of change of opacity of these gels, while the latter examined the changes in intensity of the depolarisation factors of transversely scattered light by these gel-forming mixtures during their setting.

In this investigation a study has been made of the changes in depolarisation factors and in intensity of the transversely scattered light during setting of thorium phosphate gels, prepared by the dilution method of Mehta *et al.* (*loc. cit.*).

## EXPERIMENTAL

Gelatinous precipitate of thorium phosphate was obtained by mixing adequate quantities of 10% solutions of potassium phosphate and thorium nitrate. The precipitate was washed free of impurities with hot distilled water, and dried at 110°. A saturated solution of thorium phosphate was then made in 2.96*N*-HCl. An equal volume of 2.96*N*-HCl was added to this solution; the resulting solution was filtered repeatedly through a sintered bed filter (A. G. 201×4). The strength of this stock solution was estimated as 6.740 g. $ThO_2$/litre.

A definite volume of the stock solution was taken in one test tube and in another test tube was taken a known volume of an electrolyte, diluted to such an extent that total volume of the solution after mixing was always 50 c.c. The content of one test tube was then poured into another and back again. The resulting mixture was shaken for about 30 seconds and transferred immediately to the optical cell for measurement of depolarisation and intensity of scattered light during the process of gelation. Measurements of depolarisation values $\rho_u$, $\rho_v$ and $\rho_h$, and the intensity of transversely scattered light ($I_{90}°$) were made at known intervals of time, after mixing, as described earlier (this *Journal*, 1958, **35,** 645; 1960, **37,** 282). Electrolytes used were $KNO_3$ (1.0 *M*), $K_2HPO_4$ (0.05*M*), and thorium nitrate (0.0125*M*).

The results of these measurements for one particular system are recorded in Table I in which $\rho_u$, $\rho_v$, and $\rho_h$ are expressed as percentages and the intensity values $I_{90}°$ are given in arbitrary units.

TABLE I

Thorium phosphate soln. = 1.0 c.c. Shunt = 4500 ohms. Time of setting = 12.5 mins.

| Time. | $\rho_u$. | $\rho_v$. | $\rho_h$ (calc.). | $I_{90}°$. | $I_{45}°/I_{135}°$. | Time. | $\rho_u$. | $\rho_v$. | $\rho_h$ (calc.). | $I_{90}°$. | $I_{45}°/I_{135}°$. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 min. | 8.22 | 3.96 | 86.35 | 0.50 | 3.00 | 30 min. | 3.27 | 0.85 | 34.73 | 1.25 | 3.28 |
| 3 | 5.99 | 2.65 | 75.76 | 0.60 | 3.16 | 40 | 3.27 | 0.85 | 34.73 | 1.50 | 3.42 |
| 5 | 4.71 | 1.85 | 62.76 | 0.80 | 3.20 | 50 | 3.27 | 0.85 | 34.73 | 1.75 | 3.47 |
| 7 | 4.71 | 1.85 | 62.76 | 0.90 | 3.25 | 60 | 3.27 | 0.85 | 34.73 | 1.75 | 3.47 |
| 10 | 4.71 | 1.85 | 62.76 | 1.00 | 3.28 | 80 | 3.27 | 0.85 | 34.73 | 1.75 | 3.47 |
| 15 | 4.33 | 1.51 | 52.31 | 1.00 | 3.28 | 100 | 3.27 | 0.85 | 34.73 | 1.75 | 3.47 |
| 20 | 3.61 | 1.01 | 38.31 | 1.25 | 3.28 | 120 | 3.27 | 0.85 | 34.73 | 1.75 | 3.47 |

## DISCUSSION

The data recorded in Table I indicate a decrease in the $\rho_v$ values from about 4.14 to 0.62% during setting time in the gel-forming systems containing increasing amounts of thorium phosphate as well as different amounts of electrolytes. Similar observations have been made by Ramiah (*Proc. Ind. Acad. Sci.*, 1937, **5A,** 138) in the case of silicic acid gels. These observations show that in the gel-forming system under investigation, the gel structure is being built up of particles, which are initially anisotropic in nature. As the setting of gel progresses with lapes of time, anisotropy of the particles becomes less and less until finally the particles in the set gels are very nearly isotropic in shape and/or structure.

FIG. 1

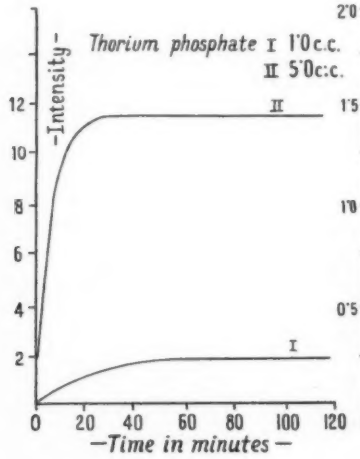
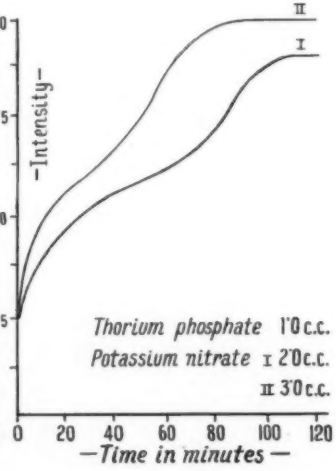



FIG. 2




It is seen further that the particles in the set gels are very nearly spherical in different systems containing increasing amounts of thorium phosphate and different electrolytes.

The $\rho_h$ values were obtained from the observed values of $\rho_u$ and $\rho_v$ using Krishnan's relation,

$$\rho_u = \frac{1 + 1/\rho_h}{1 + 1/\rho_v},$$

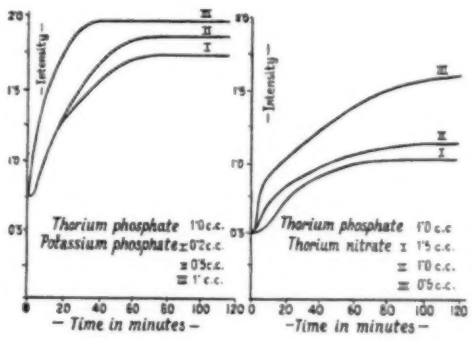
(*ibid.*, 1935, **1A,** 717, 782). It is observed that the values of $\rho_h$ show a decrease during setting of the gels, indicating commencement of agglomeration of the particles resulting in the increase

of their size. The final values of $\rho_h$ show that the size of the particles in the set gels is comparatively large with respect to the wave lengths of the incident light used.

The changes in the intensity of transversely scattered light with time are shown in Table I and in Fig. 1. It is observed that the intensity of the transversely scattered light goes on increasing with time and at a certain stage the intensity reaches a maximum ; thereafter it remains steady. These observations reveal that in the initial stage the process of agglomeration takes place which results in the increase in size, incidently in the number of the particles as well. At a certain stage, when the intensity reaches a maximum, the process of agglomeration is complete. This happens when the gel is set ; after setting there is no change in size and number of the particles, as indicated by the horizontal part of the curve.

The effect of adding electrolytes on the intensity values is clearly seen from the curves (Figs. 2-4). With increase in concentrations of $KNO_3$ and $K_2HPO_4$, the increase in the value of intensity is observed while thorium nitrate shows the reverse effect. These observations show that electrolytes ($KNO_3$, $K_2HPO_4$) help the process of agglomeration, thus causing increase in particle size while thorium nitrate facilitates peptisation.

FIG. 3 FIG. 4




*Density and Anisotropy Scattering*

The density scattering ($I_D$) and the anisotropy scattering ($I_A$) have been separated from the total intensity ($I_{90°}$) of the transversely scattered light. The values of $I_D$ and $I_A$ have been calculated from the relation (cf. Zimm *et al.*, *Polymer Bull.*, 1945, **1**, 90) :

$$I_D = I \times \frac{6 - 7\rho}{6 + 6\rho} ;$$

$$I_A = I - I_D = I \times \frac{13\rho}{6 + 6\rho}$$

and are shown in Table II.

The values of the density scattering ($I_D$) thus appear to increase with time while the anisotropy scattering ($I_A$) goes on decreasing with time during setting of the gels. The increase in the $I_D$ values shows a gradual increase in the particular size owing to agglomeration, while the decrease in $I_A$ values indicates that the particles, which are anisotropic in the beginning, become less and less anisotropic in shape and/or structure, ultimately attaining spherical shape when the gel is set.

TABLE II

Thorium phosphate soln. = 1.0 c.c. Time of setting = 8.0 mins. 1.0*M*-$KNO_3$ = 3.0 c.c.

| Time. | $\rho_v$. | $\rho = \frac{2\rho_v}{1+\rho_v}$. | $\frac{6-7\rho}{6+6\rho}$. | $I_{90}°$. | $I_D$. | $I_A$. |
|---|---|---|---|---|---|---|
| 5 min. | 2.80 | 0.0545 | 0.8882 | 0.80 | 0.7106 | 0.0894 |
| 7 | 2.37 | 0.0463 | 0.9040 | 0.90 | 0.8136 | 0.0864 |
| 10 | 1.85 | 0.0363 | 0.9158 | 1.00 | 0.9158 | 0.0842 |
| 15 | 1.85 | 0.0363 | 0.9158 | 1.00 | 0.9158 | 0.0842 |
| 20 | 1.73 | 0.0341 | 0.9270 | 1.10 | 1.0210 | 0.0790 |
| 30 | 1.30 | 0.0257 | 0.9456 | 1.20 | 1.1340 | 0.0660 |
| 40 | 1.30 | 0.0257 | 0.9456 | 1.30 | 1.2290 | 0.0710 |
| 50 | 0.93 | 0.0184 | 0.9610 | 1.50 | 1.4420 | 0.0580 |
| 60 | 0.69 | 0.0137 | 0.9709 | 2.00 | 1.9420 | 0.0580 |
| 80 | 0.69 | 0.0137 | 0.9709 | 2.00 | 1.9420 | 0.0580 |
| 100 | 0.69 | 0.0137 | 0.9709 | 2.00 | 1.9420 | 0.0580 |
| 120 | 0.69 | 0.0137 | 0.9709 | 2.00 | 1.9420 | 0.0580 |

*Dissymmetry : Ratio* $I_{45°}/I_{135°}$

The values of the ratio $I_{45°}/I_{135°}$ are shown in Table I. It will be seen that the values lie between 3.0 and 5.5. It appears from these observations that the particles are initially disc-shaped. The data, obtained from the depolarisation factor $\rho_v$, indicate, however, the possibility of the particles attaining more or less spherical shape in the set gels. The dissymmetry: ratio $I_{45°}/I_{135°}$ does not give true indication of the probable shape of the particles in these gel-forming systems.

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# β-Phenylethanol Amines. Part II*. Studies on Cyclodehydration of a Few Acylamino Alcohols

**N. Adityachaudhury, S. K. Srimany, and (Mrs.) A. Chatterjee**

Cyclodehydration of some acylamino alcohols to their corresponding isoquinolines has been studied. *N*-[β-hydroxy-β(3, 4-methylenedioxyphenyl)ethyl]-cinnamamide and its dihydro derivative yield readily the corresponding isoquinoline derivatives, viz., 1-(styryl)-6, 7-methylenedioxy- and 1-(β-phenyl)ethyl-6, 7-methylenedioxy-isoquinolines, whereas *N*-[β-hydroxy-β-(*p*-methoxyphenyl)ethyl] -cinnamamide and its dihydro derivative fail to cyclise when subjected to the Bischler-Napieralski reaction. During this reaction *N*-[β-hydroxy-β-(*p*-methoxyphenyl)ethyl]-cinnamamide suffers degradation to *trans*-cinnamamide and a dark brown styrene polymer.

In a previous communication (Adityachaudhury and Chatterjee, this *Journal*, 1959, **36**, 585) a new method for the preparation of various β-phenylethanol amines and its extension in the syntheses of an acylamino alcohol, viz., aegeline, *dl-trans-N*-[β-hydroxy-β-(*p*-methoxyphenyl)ethyl]-cinnamamide, and an isoquinoline base, papaverine, has been described.

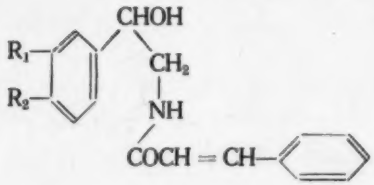
Since isoquinoline alkaloids are generally synthesised from acylamino derivatives of β-phenylethyl or ethanol amines, it was thought interesting to investigate whether (*a*) aegeline, *N*-[β-hydroxy-β-(*p*-methoxyphenyl)ethyl]-cinnamamide (I), (*b*) dihydroaegeline, *N*-[β-hydroxy-β-(*p*-methoxyphenyl)ethyl]-dihydrocinnamamide, and other two similar amides, viz., (*c*) *N*-[β-hydroxy-β-(3, 4-methylenedioxyphenyl)ethyl]-cinnamamide (II) and its dihydro derivative, (*d*) *N*-[β-hydroxy-β-(3, 4-methylenedioxyphenyl)ethyl]-dihydrocinnamamide, all having requisite acylamino structures, can be cyclised by the Bischler-Napieralski reaction to the corresponding isoquinolines. Studies on cyclodehydration of these amides are described in this communication. It seems pertinent to mention that the amides (*c*) and (*d*) have been synthesised for the first time by the present investigators.

*N*-[β-Hydroxy-β-(3, 4-methylenedioxyphenyl)ethyl]-cinnamamide (II) was prepared by the condensation of β-hydroxy-β-3, 4-methylenedioxyphenylethyl amine (Adityachaudhury and Chatterjee, *loc. cit.*) with cinnamoyl chloride. The amide crystallised from acetone in fine needles, m.p. 176-77°. The amide on hydrogenation with Adams' catalyst afforded *N*-[β-hydroxy-β-(3,4-methylenedioxyphenyl)ethyl]-dihydrocinnamamide, m.p. 134-36°.

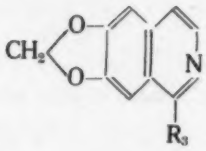
Cyclisation of the amide (II) with phosphorus oxychloride in dry toluene furnished 1-(styryl)-6,7-methylenedioxyisoquinoline (III) in fairly good yield. The base was obtained as an oil, which was converted into its picrate, m.p. 230-31° (decomp.). This isoquinoline base is not known in the literature. The picrate shows characteristic absorption maxima in the UV region at 252 (log ε, 4.01), 279 (log ε, 3.73), and 313 mμ (log ε, 3.64) in ethanol.

*N*-[β-Hydroxy-β-(3,4-methylenedioxyphenyl)ethyl]-dihydrocinnamamide, when cyclised over phosphorus oxychloride in dry toluene, afforded 1-(β-phenyl)ethyl-6,7-methylenedioxyisoquinoline (IV) in good yield. The base was purified by chromatography over Brockmann alumina, followed by crystallisation from methanol, in shining colorless rods, m.p. 83-85°. The base exhibits characteristic absorption maxima in the UV region at 238 (log ε, 4.72), 278 (log ε, 3.72), 316 (log ε, 3.62), and 329 mμ (log ε, 3.71) in ethanol. The hydrobromide of the base (IV) was crystallised from methanol in glistening needles, m.p. 253-54° (decomp.).

* Part I: This *Journal*, 1959, **36**, 585.



(I): $R_1 = H$ ; $R_2 = OMe$.
(II): $R_1 = R_2 = O-O$ ($CH_2$).



(III): $R_3 = -CH = CH.Ph$.
(IV): $R_3 = -CH_2.CH_2.Ph$.

The extension of the above method of cyclisation in case of aegeline (I) and dihydroaegeline met with failure. Both these amides turned brown spontaneously when treated with phosphorus oxychloride and phosphorus pentoxide and yielded a dark brown resinous mass on heating for 10 to 15 minutes. The reaction products after being processed for the corresponding isoquinolines did not give positive tests with alkaloidal reagents, indicating the failure of ring closure. The neutral fraction from cyclodehydration products of aegeline yielded a compound, which crystallised from benzene in fine needles, m.p. 140-41° (yield 10%). The latter fits the formula $C_9H_9ON$. It was characterised as *trans*-cinnamamide. Formation of *trans*-cinnamamide during the cyclodehydration of aegeline obviously indicates that the other fragment of the alkaloid-amide is a styrene derivative. The latter, however, underwent a rapid polymerisation into a dark resinous mass. It might be recalled (McCoubrey and Mathieson, *J. Chem. Soc.*, 1949, 696) that during cyclisation of the benzoyl derivatives of *m*- and *p*-nitrophenylethyl amines, considerable proportions of the corresponding *m*- and *p*-nitrophenyl cyanides were formed as byproducts. The reason for failure of cyclisation is possibly due to inductive deactivation of the methoxyl group in aegeline (I) and dihydroaegeline, *meta* to the point of ring closure. In fact, the amides derived from 2,4-dimethoxyphenylethyl amine and 2,4-dimethoxyphenylisopropyl amine fail to yield the corresponding 3,4 dihydroisoquinolines by the Bischler-Napieralski reaction (Govindachari and Lakshmikantham, *Proc. Ind. Acad. Sci.*, 1957, **46A**, 414).

## *EXPERIMENTAL

N-[β-*Hydroxy*-β-(3,4-*methylenedioxyphenyl*)*ethyl*]-*cinnamamide*.—An ethereal solution (20 c.c.) of cinnamoyl chloride (3 g.) was added dropwise to β-hydroxy-3,4-methylenedioxyphenylethyl amine (3 g.), prepared by a new method described previously (*loc. cit.*), and dissolved in the same solvent (30 c.c.) with constant shaking, when the amide was precipitated. A cold aqueous 10% solution of NaOH (30 c.c.) was added towards the end of the reaction. The amide was filtered, washed several times with water, and crystallised from acetone in fine needles (3.2 g.), m.p. 176-77°. (Found : C, 69.52 ; H, 5.39. $C_{18}H_{17}O_4N$ requires C, 69.43 ; H, 5.45%).

N-[β-*Hydroxy*-β-(3,4-*methylenedioxyphenyl*)*ethyl*]-*dihydrocinnamamide*.—The preceding amide (2 g.) on hydrogenation with Adams' catalyst (0.3 g.) for 2 hours in aldehyde-free ethanol (300 c.c.) showed an uptake of one mole of hydrogen. The solution was filtered and concentrated, when the desired amide was obtained. It was crystallised from acetone in glistening colorless needles (1.75 g.), m.p. 134-36°. (Found : C, 69.15 ; H, 6.26. $C_{18}H_{19}O_4N$ requires C, 69.00 ; H, 6.06%).

*Dihydroaegeline*.—Aegeline (2 g.) was hydrogenated with Adams' catalyst for 2 hours in aldehyde-free ethanol (250 c.c.), when it showed an uptake of one mole of hydrogen. Dihydroaegeline (1.8 g.) was crystallised from a mixture of ethanol and ethyl acetate in colorless plates, m.p. 140°. (Found : C, 72.34 ; H, 7.14. Calc. for $C_{18}H_{21}O_3N$ : C, 72.24 ; H, 7.02%).

* All m.p.s. are uncorrected.

*Cyclisation of* N-[β-*Hydroxy*-β-(3,4-*methylenedioxyphenyl*)*ethyl*]-*cinnamamide.*—A solution of the amide (1.5 g.) in dry toluene (8 c.c.) and $POCl_3$ (7 c.c.) were refluxed at 110° for 2 hours. The reaction product was poured into crushed ice. The aqueous layer was separated and the toluene layer extracted with 4*N*-HCl (4 × 10 c.c.). The combined acid extract was washed with ether and the acidic aqueous solution was thoroughly cooled and basified with dilute $NH_4OH$ solution. The liberated base was extracted with ether (3 × 50 c.c.), washed with water, dried over anhydrous potassium carbonate, and the solvent removed, when the desired 1-(styryl)-6,7-methylenedioxyisoquinoline was obtained as a pale yellow liquid (0.51 g.). The base was characterised as its picrate.

*Picrate of* 1-(*styryl*)-6,7-*methylenedioxyisoquinoline* was prepared by adding a saturated ethereal solution of picric acid (0.2 g. in 10 c.c.) to an ethereal solution of the base (0.2 g. in 5 c.c.). The resulting yellowish brown picrate was crystallised from methanol in fine, shining needles, m.p. 230-31° (decomp.). (Found : C, 57.42 ; H, 3.41 ; N, 11.31. $C_{24}H_{16}O_9N_4$ requires C, 57.14 ; H, 3.11 ; N, 11.11%).

*Cyclisation of* N-[β-*Hydroxy*-β-(3,4-*methylenedioxyphenyl*)*ethyl*]-*dihydrocinnamamide.*—A mixture of the amide (1.0 g.) in dry toluene (30 c.c.) and $POCl_3$ (6 c.c.) was refluxed at 110° for an hour. The solvent was removed in *vacuo* and the residue extracted with 4*N*-HCl (4×25 c.c.). The combined acid extract was well cooled and basified with an aqueous 10% solution of NaOH (75 c.c.). The liberated base was extracted with ether (6 × 50 c.c.) ; the extract (300 c.c.) was washed with water, dried over anhydrous sodium sulphate, and concentrated, when the base was obtained as a solid (0.65 g.). This synthetic base, 1-(β-phenyl)ethyl-6,7-methylenedioxyisoquinoline, was purified by chromatographic resolution over a column (6 cm ×1 cm) of Brockmann alumina using benzene as a developer. Fractions were collected in 15 c.c. portion, each (Table I).

TABLE I

| Eluent. | Fractions. | Residue on evaporation. |
|---|---|---|
| Benzene | 1-3 | Oily residue |
| " | 4-6 | Colorless rods; m.p. 82-84° |
| " | 7-8 | Nil |

Fractions 4-6 were crystallised from benzene in rods, m.p. 83-85°. (Found : C, 77.76 ; H, 5.56 ; N, 4.95. $C_{18}H_{15}O_2N$ requires C, 77.97 ; H, 5.41 ; N, 5.05%).

*Hydrobromide of* 1-(β-*phenyl*)*ethyl*-6,7-*methylenedioxyisoquinoline* was prepared by dissolving the base (0.2 g.) in methanol (5 c.c.) and adding a few drops of aqueous hydrobromic acid (48%), when colorless, shining needles separated. These were crystallised from methanol, m.p. 252-53° (decomp.). (Found : N, 4.08. $C_{18}H_{15}O_2N.HBr$ requires N, 3.9%).

*Attempted Cyclisation of Aegeline.*—A mixture of aegeline (1.0 g.), suspended in dry xylene (25 c.c.), and $POCl_3$ (5.0 g.) after being refluxed for 10 minutes was poured into crushed ice. After some time, the aqueous layer was separated and the xylene layer extracted with 4*N*-HCl (4 × 10 c.c.). The combined aqueous acid extract was shaken once with ether (50 c.c.) and made neutral with sodium bicarbonate, when a white solid separated. The latter was extracted with ether (4 × 25 c.c.). The ether extract (A) was washed with water, dried over anhydrous sodium sulphate, and the solvent removed. The aqueous solution was basified with $NH_4OH$ solution and extracted with ether (3 × 25 c.c.). The ether extract (B) on evaporation left no residue.

The neutral compound, isolated from ether extract (A), was crystallised from benzene in shining needles (0.12 g.), m.p. 138-39°. It was further purified by chromatographic resolution over Brockmann alumina (5.0 g.) using the following as developers (Table II). Fractions were collected in 25 c.c. portion, each.

TABLE II

| Eluents. | Fractions. | Residue on evaporation. |
|---|---|---|
| Petroleum ether (b.p. 60-80°) | 1-3 | Oily residue, not crystallisable. |
| Benzene | 4-8 | Colorless needles, m.p. 140-41°. |
| ,, | 9-11 | Nil |

Fractions 4-8 on recrystallisation from benzene furnished colorless needles, m.p. 140-41°. (Found : C, 73.54 ; H, 6.14 ; N, 9.49. Calc. for $C_9H_9ON$ : C, 73.46 ; H, 6.12 ; N, 9.52%).

The neutral substance was found to be *trans*-cinnamamide from its analysis, and m.p. and mixed m.p. determinations with a synthetic sample of cinnamamide (*trans*).

*Attempted Cyclisation of Dihydroaegeline.*—Dihydroaegeline was subjected to cyclodehydration under the same experimental condition as described for aegeline. No alkaloidal material could be isolated from the reaction mixture.

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# A Study on Complex Formation of Beryllium with Salicylic and Sulphosalicylic Acids

**Rebati Charan Das and S. Aditya**

Beryllium perchlorate ($Be^{2+}$) forms a colorless complex with salicylic acid as well as with sulphosalicylic acid. The nature of these complexes has been studied by ultraviolet spectrophotometry. The absorption spectra at different *p*H's suggest that the complex formation increases with an increase in *p*H. Composition of these complexes has been studied at *p*H 4.5 by Job's method of continued variation. The molecular ratio of $Be^{2+}$ to the ligand in both the complexes is 1 : 1. Stability constants have been determined at ionic strengths 0.02, 0.05, 0.1, and 0.2*M* for the $Be^{2+}$ -salicylic acid complex as well as for the $Be^{2+}$-sulphosalicylic acid complex. Thermodynamic stability constants have been found by extrapolation and are $1.66\times10^4$ and $2.24\times10^4$ for salicylic acid and sulphosalicylic acid complexes respectively; the values of $-\Delta F$'s are 5830 and 6010 cals. respectively.

Meeks and Bank (*J. Amer. Chem. Soc.*, 1951, **73,** 4108) studied spectrophotometrically the complex formed by $Be^{2+}$ with sulphosalicylic acid at *p*H 4.5. Verma and Mehrotra (this *Journal*, 1958, **35,** 380) studied the nature of beryllium-salicylic acid complex by electrometric and conductometric titrations. In the present work the nature of the complexes formed by beryllium with salicylic and sulphosalicylic acids has been investigated spectrophotometrically at a lower *p*H range ; the stability constants have also been determined.

## EXPERIMENTAL

Beryllium perchlorate was prepared by dissolving B.D.H. beryllium carbonate in pure perchloric acid solution. Sufficient free acid was present in the solution to prevent hydrolysis of the metal ion. Beryllium content was estimated by precipitating the hydroxide and subsequently heating it to oxide (Vogel, "Textbook of Quantitative Inorganic Analysis", 2nd ed., p. 450).

Both salicylic and sulphosalicylic acids were of E. Merck G. R. quality. The stock solutions were prepared by dissolving in double-distilled water and were estimated by titration against standard alkali. Sodium perchlorate (B.D.H.) was used to maintain the ionic strength. All other chemicals were of Reagent grade.

The solutions for the measurements were prepared by taking required volumes of beryllium perchlorate and the ligand solutions from the stock. Requisite amounts of alkali or acid and sodium perchlorate were added before dilution to maintain the *p*H and the ionic strength respectively in the same way as reported earlier (Das and Aditya, this *Journal*, 1960, **37,** 557).

Absorbancies were measured with a Hilger-Watt 'Uvispek' spectrophotometer, model H 700/303, using quartz cells of 10 mm path length. Duplicate readings were taken for each solution by taking measurements with cells interchanged. The slit width was adjusted corresponding to a band width of 5 Å. The *p*H measurements were made with a Marconi *p*H meter, model TF 511 D. The experiments were done at room temperature, which varied between 28° and 32°.

## DISCUSSION

Salicylic acid has an absorption maximum at 296 mμ. The addition of beryllium perchlorate shifts the maximum to 305 mμ at *p*H 4.5. A similar shift from 297 mμ to 304 mμ was also observed with sulphosalicylic acid. Figure 1 shows the absorption curves of salicylic acid at *p*H 3.0 and 4.5 and those of a solution of salicylic acid and beryllium ion at the same *p*H values. *p*H 4.5 was thus chosen for further work.

### *Composition of the Complexes*

For determination of molecular composition of the complexes Job's method of continued variation (*Compt. rend.*, 1928, **180,** 928; *Ann. chim.*, 1928, *x*, **9,** 113) was used. Figure 2 represents the continued variation curve for $Be^{2+}$-salicylic acid system. At wave length 315 mμ the curve passes through a maximum, while at 285 mμ it passes through a minimum. Both the curves indicate a complex between $Be^{2+}$ and salicylic acid in the ratio of 1 : 1. The curves at wave lengths 310 mμ and 320 mμ also have the maximum at the molecular ratio of 1 : 1. In the case of sulphosalicylic acid system, the continued variation curve passes through a minimum at the wave length 285 mμ and maxima at other three wave lengths. In this case also the molecular ratio of beryllium to the ligand in the complex is 1 : 1 at the above *p*H. That not more than one complex is formed at *p*H 4.5 is assumed from the fact that the maxima or minima of the Job's curves remain unchanged at all wave lengths (Vosburgh and Cooper, *J. Amer. Chem. Soc.*, 1941, **63,** 487).

FIG. 1

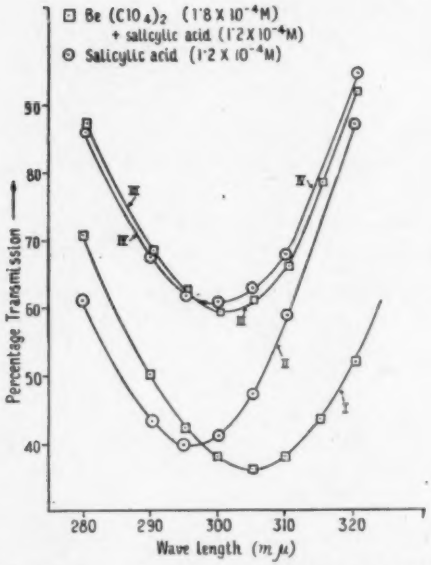
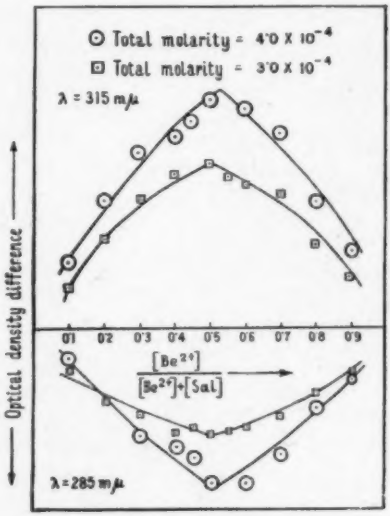



FIG. 2




Curves I & II—Actual % T = % T from graph (*p*H 4.5)
Curves III & IV—Actual % T=% T from graph −20 (*p*H 3.0)

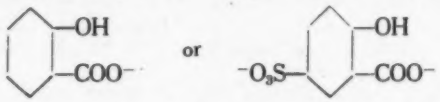
### *Extinction Coefficient*

Extinction coefficients of the beryllium complexes were determined by measuring optical densities of the solutions at wave length 315 mμ and at *p*H 4.5, with beryllium ion concentrations in 20 to 30 folds excess, when the complex formation was assumed to be complete and the absorbancies were entirely due to the complexes formed. The values for the extinction coefficients of $Be^{2+}$-salicylic acid and $Be^{2+}$-sulphosalicylic acid complexes at *p*H 4.5 and at wave length 315 mμ were found to be $4468 \pm 12$ and $3996 \pm 5$ respectively as against $1184 \pm 2.6$ and $984 \pm 1.3$ respectively for the ligands.

*Stability Constants*

For determination of stability constants, absorbancies of the solutions containing beryllium perchlorate and the ligand, with *p*H adjusted to 4.5, were measured at wave length 315 mμ. Requisite amounts of sodium perchlorate were added to these to fix the ionic strengths. The ionic strength was calculated from the amount of sodium perchlorate added as the concentration was large in comparison with that of any other constituent in the solution. Calculation of the stability constant was done in the following manner.

At *p*H 4.5, both the ligands, salicylic and sulphosalicylic acids, exist in the form :




(which is represented as HR). The reaction equilibrium can then be represented as :

$$Be^{2+} + HR = BeR + H^{+}.$$

At constant $H^{+}$-ion concentration,

$$\frac{[BeR]}{[Be^{2+}]\,[HR]}$$

is a constant ($K$). The concentration of [HR] is equal to $[HR]_T - [BeR]$, where $[HR]_T$ is the total concentration of the ligand and [BeR] is the concentration of the ligand bound in the complex. Similarly, the concentration of the free beryllium ion is given by $[Be^{2+}]_T - [BeR]$. Thus the association constant is given by the expression :

$$K = \frac{[BeR]}{\{[Be^{2+}]_T - [BeR]\}\,\{[HR]_T - [BeR]\}}.$$

The concentration of the complex, *i.e.*, [BeR] in the above equation, is calculated from the optical density of the solution containing $Be^{2+}$ ion and the ligand, using the expression,

$$\text{Optical density} = \epsilon_2\,[BeR]\,l + \epsilon_1\,\{[HR]_T - [BeR]\}\,l,$$

where $\epsilon_2$ and $\epsilon_1$ are the extinction coefficients of the complex and the ligand respectively and '$l$', the cell width.

At each ionic strength ten sets of optical density measurements were taken with solutions containing different amounts of the metal ion and the ligand. The number of measurements taken and the average association constants with standard deviations from the same are shown in Table I.

TABLE I

*Stability constant of* Be-*salicylic acid and* Be-*sulphosalicylic acid complexes.* *p*H = 4.5. No. of readings taken with varying conc. of Be and ligand = 10.

| Ionic strength. | Mean value of $K \times 10^{-4}$ for the complex with | |
|---|---|---|
| | Salicylic acid. | Sulphosalicylic acid. |
| 0.02 | 1.205 ± 0.11 | 1.960 ± 0.20 |
| 0.05 | 1.008 ± 0.09 | 1.715 ± 0.17 |
| 0.10 | 0.937 ± 0.07 | 1.501 ± 0.18 |
| 0.20 | 0.900 ± 0.09 | 1.470 ± 0.15 |

An analysis of the results shows that with an increase in the ionic strength the stability constant decreases.

For calculation of the thermodynamic association constants, the values of the activity coefficients of different species in solution are necessary. Since it is difficult to determine them experimentally and also it is not possible to get them theoretically, the thermodynamic association constants ($K_T$) have been found by extrapolating the curve (log $K$ against ionic strength) to zero ionic strength. The values of $K_T$'s for the salicylic and sulphosalicylic acid complexes of beryllium are $1.66\times10^4$ and $2.24\times10^4$ respectively. Taking the average temperature (at which the experiments were done) to be $30°\pm2°$, the values of $-\Delta F$'s for the complexes were calculated. For the $Be^{2+}$— salicylic acid complex, it is 5830 cals. and for the $Be^{2+}$— sulphosalicylic acid complex, it is 6010 cals.

As can be observed from the values of stability constants, sulphosalicylic acid forms a stronger complex with beryllium ion than salicylic acid. Similar observations were made by us in connection with our studies on complexes of $Al^{3+}$, $Ga^{3+}$, and $Fe^{3+}$ (unpublished).

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# Studies on 2-*o*-Anisylimino-3-*o*-anisyl-4-thiazolidone, 3-*o*-Anisyl-2, 4-thiazolidione, 2-*o*-Phenetylimino-3-*o*-phenetyl-4-thiazolidone, 3-*o*-Phenetyl-2, 4-thiazolidione, and the Fungicidal Activity of the Acetoxymercuri Derivatives of the Thiazolidiones

**P. N. Bhargava, Miss Kamalini Bhargava, and R. C. Kapoor**

2-*o*-Anisylimino-3-*o*-anisyl-4-thiazolidone, 3-*o*-anisyl-2,4-thiazolidione, 2-*o*-phenetylimino-3-*o*-phenetyl-4-thiazolidone, and 3-*o*-phenetyl-2, 4-thiazolidione have been synthesised and their characteristic reactions studied. The fungicidal activity of the acetoxymercuri derivatives of these thiazolidiones has been tested.

In continuation of our earlier work on 3-*m*-tolyl-2,4-thiazolidione and 5-arylazo-3-phenyl-2-phenylimino-4-thiazolidones (Bhargava *et al.*, this *Journal*, 1957, **34**, 475), it was considered worthwhile to prepare 2-*o*-anisylimino-3-*o*-anisyl-4-thiazolidone, 3-*o*-anisyl-2,4-thiazolidione, 2-*o*-phenetylimino-3-*o*-phenetyl-4-thiazolidone, and 3-*o*-phenetyl-2,4-thiazolidione and to test the fungicidal activity of the acetoxymercuri derivatives of the thiazolidiones, referred to above.

The two new thiazolidones have been prepared by interaction of the respective *S*-di-*o*-anisylthiourea and *S*-di-*o*-phenetylthiourea with monochloroacetic acid in ethanol in presence of anhydrous sodium acetate. The reactive methylene group of 2-*o*-anisylimino-3-*o*- anisyl-4-thiazolidone has been condensed with five aromatic aldehydes, and that of 3-*o*-anisyl-2,4-thiazolidione with four aromatic aldehydes, yielding 5-arylidene derivatives.

Mercuration of 3-*o*-anisyl-2,4-thiazodione with mercuric acetate has yielded a mercuri derivative, presumably 3-acetoxymercuri-*o*-anisyl-2, 4-thiazolidione. The acetoxymercuri group is expected to enter the aryl nucleus. Again, the reactive methylene group of 2-*o*-phenetylimino-3-*o*-phenetyl-4-thiazolidone has been condensed with five aromatic aldehydes and two aryldiazonium chlorides, yielding respectively 5-arylidene and 5-arylazo-substituted thiazolidones. Similarly the active methylene group of 3-*o*-phenetyl-2,4-thiazolidione has also been condensed with four aromatic aldehydes and two aryldiazonium chlorides.

The attachment of the azo group to $-CH_2-$ group in position 5 in α-position to the activating carbonyl group is justified by the arguments advanced by Meerwein *et al.* (*J. prakt. Chem.*, 1939, **152**, 237) and is further supported by the observation that when the $-CH_2-$ group in position 5 of the thiazolidone or thiazolidione nucleus is blocked by condensation with aromatic aldehydes, no azo dye is formed. The latter thiazolidione on mercuration has yielded 3-acetoxymercuri-*o*-phenetyl-2, 4-thiazolidione.

Further, 2-*o*-phenetylimino-3-*o*-phenetyl-4-thiazolidone and 3-*o*-phenetyl-2, 4-thiazolidione on oxidation with $KMnO_4$ in glacial acetic acid have yielded the corresponding sulphones, as confirmed by analytical data.

Finally, 3-acetoxymercuri-*o*-anisyl-2, 4-thiazolidione, when tested for its fungicidal activity against the fungus *Alternaria solani*, has been found to inhibit completely the germination up to 66 p.p.m. Similarly, 3-acetoxymercuri-*o*-phenetyl-2, 4-thiazolidione, when tested against the fungus *Fusarium navile*, has been found to check germination of the spores up to a concentration of 26.58 p.p.m.

## EXPERIMENTAL

*2-o-Anisylimino-3-o-anisyl-4-thiazolidone* was prepared according to the method of Klare *et al.* (*J. Amer. Chem. Soc.*, 1930, **52,** 2137) under conditions laid down by Bhargava and Kaul (this *Journal*, 1955, **38,** 49) in a colorless crystalline form, m.p. 196.5°, maximum yield 81% under the optimum period of heating for 13.5 hours. (Found : S, 9.60. $C_{17}H_{16}O_3N_2S$ requires S, 9.64%).

*2-o-Phenetylimino-3-o-phenetyl-4-thiazolidone* was obtained similarly, as above, in a dull yellow form, m.p. 118° ; maximum yield 81.69% under optimum period of heating of 3 hours. (Found : S, 9.18. $C_{19}H_{20}O_3N_2S$ requires S, 8.78%).

*3-o-Anisyl-2, 4-thiazolidione* was prepared according to Klare *et al.* (*loc. cit.*) as white needles, m.p. 113.5°; maximum yield 50% under optimum period of heating of 11 hours. (Found : S, 14.29. $C_{10}H_9O_3NS$ requires S, 14.35%).

*3-o-Phenetyl-2, 4-thiazolidione* was obtained similarly in a yellow crystalline form, m.p. 84° ; maximum yield 30.8% after a heating period of 4.5 hours. (Found : S, 13.35. $C_{11}H_{11}O_3NS$ requires S, 13.5%).

*2-o-Anisylimino-3-o-anisyl-5-benzylidene-4-thiazolidone.*—A mixture of thiazolidone (0.4 g.), benzaldehyde (0.2 c.c.), and pyridine (150 c.c.) were refluxed in an oil bath at 135° for 6 hours. After the reaction the substance was crystallised in a dull yellow crystalline form, m.p. 169°.

Similarly other aldehydes were condensed, yielding 5-arylidene derivatives. Physical properties and analytical data are recorded in Table I.

*2-o-Phenetylimino-3-o-phenetyl-5-benzylidene-4-thiazolidone* was obtained according to the procedure, mentioned above, by heating in an oil bath at 160° for 3.5 hours. The properties and analytical data of 5-arylidene derivatives obtained by condensation with other aldehydes are mentioned in Table I.

*3-o-Anisyl-5-benzylidene-2, 4-thiazolidione.*—A mixture of thiazolidione (0.446 g.), benzaldehyde (0.212 g.), dissolved in glacial acetic acid (10 c.c.), and anhydrous sodium acetate (1.0 g.) was heated under reflux for 1.5 hours. On pouring the contents into water and keeping overnight, a yellow precipitate was obtained, which was crystallised from ethanol as yellow needles, m.p. 98°. Similarly other aldehydes were condensed, yielding 5-arylidene derivatives. The properties and analytical data are recorded in Table II.

*3-o-Phenetyl-5-benzylidene-2, 4-thiazolidione* was prepared according to the above method. Similarly other aldehydes were condensed with the thiazolidione. The properties and analytical data are recorded in Table II.

*2-o-Phenetylimino-3-o-phenetyl-5-phenylazo-4-thiazolidone* was prepared by the method of Bhargava and Goswami (this *Journal*, 1955, **32,** 763). The thiazolidone was likewise condensed with *p*-toluenediazonium chloride. The properties of these compounds and their analytical data are recorded in Table III. Similarly 5-arylazo derivatives of 3-*o*-phenetyl-2,4-thiazolidione were prepared as reported in Table III.

*2-o-Phenetylimino-3-o-phenetyl-4-thiazolidone Sulphone.*—2-*o*-Phenetylimino-3-*o*-phenetyl-4-thiazolidone (1 g.) was dissolved in glacial acetic acid (20 c.c.) and treated slowly with $KMnO_4$ (1 g.), dissolved in water (40 c.c.), at 0°. The precipitate obtained after removing excess of $KMnO_4$ and chilling was washed with ice-cold water, dried, and crystallised from ethanol in a yellow form, m.p. 106°. (Found : S, 8.18. $C_{19}H_{20}O_5N_2S$ requires S, 8.25%).

TABLE I

2-o-*Anisylimino*-3-o-*anisyl*-5-*arylidene*-4-*thiazolidones* (A) *and* 2-o-*phenetylimino*-3-o-*phenetyl*-5-*arylidene*-4-*thiazolidones* (P).

| | A-4-thiazolidones. | | | | | P-4-thiazolidones. | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Aldehyde. | Colour. | M.P. | Formula. | % Sulphur. Found. | Calc. | Colour. | M.P. | Formula. | % Sulphur. Found. | Calc. |
| Benzaldehyde | Yellow | 169° | $C_{24}H_{20}O_3N_2S$ | 7.60 | 7.63 | Pale yellow | 121° | $C_{26}H_{24}O_3N_2S$ | 7.10 | 7.20 |
| *m*-Hydroxybenzaldehyde | Grey | 145° | $C_{24}H_{20}O_4N_2S$ | 7.32 | 7.40 | .. | .. | .. | .... | |
| *p*-Hydroxybenzaldehyde | Yellow | 138° | $C_{24}H_{20}O_4N_2S$ | 7.36 | 7.40 | Yellow | 135° | $C_{26}H_{24}O_4N_2S$ | 6.90 | 6.95 |
| *o*-Chlorobenzaldehyde | .. | .. | .. | .. | .. | Pale yellow | 119° | $C_{26}H_{23}O_3N_2ClS$ | 6.58 | 6.69 |
| *p*-Anisaldehyde | Chocolate | 161° | $C_{25}H_{22}O_4N_2S$ | 7.01 | 7.17 | .. | .. | .. | .... | |
| Cinnamaldehyde | .. | .. | .. | .. | .. | Yellow | 120° | $C_{28}H_{26}O_3N_2S$ | 6.70 | 6.80 |
| Furfuraldehyde | Grey | 196° | $C_{22}H_{16}O_4N_2S$ | 7.73 | 7.88 | Brown | 122° | $C_{24}H_{22}O_4N_2S$ | 7.26 | 7.37 |

TABLE II

3-o-*Anisyl*-5-*arylidene*-2, 4-*thiazolidiones* (A′) *and* 3-o-*phenetyl*-5-*arylidene*-2, 4-*thiazolidiones* (P′).

| | A′-2:4-thiazolidiones. | | | | | P′-2:4-thiazolidiones. | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Aldehyde. | Colour. | M.P. | Formula. | % Sulphur. Found. | Calc. | Colour. | M.P. | Formula. | % Sulphur. Found | Calc. |
| Benzaldehyde | Yellow | 98° | $C_{17}H_{13}O_2NS$ | 10.16 | 10.28 | Yellow | 139° | $C_{18}H_{15}O_2NS$ | 9.78 | 9.85 |
| *m*-Hydroxybenzaldehyde | Do | 118° | $C_{17}H_{13}O_3NS$ | 9.62 | 9.79 | .. | .. | .. | .. | .. |
| *p*-Hydroxybenzaldehyde | Grey | 111° | $C_{17}H_{13}O_3NS$ | 9.68 | 9.79 | .. | .. | .. | .. | .. |
| *o*-Chlorobenzaldehyde | .. | .. | .. | .. | .. | Yellow | 159° | $C_{18}H_{14}O_2NClS$ | 8.75 | 8.90 |
| Cinnamaldehyde | .. | .. | .. | .. | .. | Do | 120° | $C_{20}H_{17}O_2NS$ | 9.01 | 9.12 |
| Furfuraldehyde | Brown | 75° | $C_{15}H_{11}O_3NS$ | 9.99 | 10.63 | Brown | 132° | $C_{16}H_{13}O_3NS$ | 10.24 | 10.01 |

TABLE III

2-o-*Phenetylimino*-3-o-*phenetyl*-5-*arylazo*-4-*thiazolidone* (P″) *and* 3-o-*phenetyl*-5-*arylazo*-2, 4-*thiazolidione* (P‴).

| | P″2-4-thiazolidone. | | | | | P‴-2:4-thiazolidione. | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Diazonium chloride of amines. | *Colour in acetic acid. | M.P. | Formula. | % Sulphur. Found. | Calc. | *Colour. | M.P. | Formula. | % Sulphur. Found. | Calc. |
| Aniline | Reddish yellow | 118° | $C_{22}H_{24}O_2N_4S$ | 6.70 | 6.95 | Brown | 113° | $C_{17}H_{13}O_2N_2S$ | 9.21 | 9.38 |
| *p*-Toluidine | Orange | 121° | $C_{24}H_{28}O_2N_4S$ | 6.61 | 6.75 | .. | .. | .. | .. | .. |
| *p*-Phenetidine | .. | .. | .. | .. | .. | Reddish yellow | 126° | $C_{19}H_{19}O_4N_2S$ | 8.18 | 8.31 |

* In acetic acid.

3-o-*Phenetyl*-2, 4-*thiazolidione sulphone* was prepared and crystallised, as above, in a pale yellow form, m.p. 114°. (Found : S, 11.65. $C_{11}H_{11}O_5NS$ requires S, 11.90).

3-*Acetoxymercuri*-o-*anisyl*-2, 4-*thiazolidione*.—To the thiazolidione (1 g.), dissolved in glacial acetic acid (20 c.c.), were added ethanol (15 c.c.) and mercuric acetate (1.5 g.), dissolved in water (15 c.c.) and acidified with acetic acid. After stirring and keeping for 24 hours, a cream-coloured precipitate was obtained, which was filtered, washed with water, dried, and crystallised from ethanol in a yellow form, m.p. 116.5°. (Found : Hg, 41.94. $C_{12}H_{11}O_5NSHg$ requires Hg, 41.66%).

3-*Acetoxymercuri*-o-*phenetyl*-2, 4-*thiazolidione* was similarly prepared, as above, in an ash-coloured form, m.p. 102°. (Found : Hg, 40.68. $C_{13}H_{13}O_5NSHg$ requires Hg, 40.44%).

*Fungicidal Test*

3-*Acetoxymercuri*-o-*anisyl*-2, 4-*thiazolidione* was tested for its fungicidal activity on the spores of *Alternaria solani*, parasitic upon *Solanum tuberosum*, Linn, according to the method outlined by Horsefall (*Phytopath.*, 1940, **30,** 545) at 20°. The compound is found to be toxic as shown by the inhibition of germination in its presence. It inhibits germination completely up to 66 p.p.m., which is the minimum effective concentration. At 50 and 40 p.p.m., the spore germination is 56% and 84% respectively and below the concentration 33 p.p.m., its activity is nil. The results are tabulated in Table IV.

TABLE IV

| Sl. No. | % Conc. | Conc. | Number of spores germinated. | Number of spores ungerminated. | % Germination. |
|---|---|---|---|---|---|
| 1. | 0.100000 g. | 1000.00 p.p.m. | 0 | 150 | 0 |
| 2. | 0.010000 | 100.00 | 0 | 150 | 0 |
| 3. | 0.006667 | 66.67 | 2 | 148 | 1.3 |
| 4. | 0.005555 | 55.55 | 33 | 117 | 22 |
| 5. | 0.005000 | 50.00 | 84 | 66 | 56 |
| 6. | 0.004000 | 40.00 | 126 | 24 | 84 |
| 7. | 0.003333 | 33.33 | 150 | 0 | 100 |

3-*Acetoxymercuri*-o-*phenetyl*-2, 4-*thiazolidione*.—The test was carried on thirty days' old spores of *Fusarium navile* at 20° according to the procedure mentioned above. It has been observed that germination of spores up to 1/35,000 dilution or up to a concentration of 26.58 p.p.m. is completely inhibited.

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# Studies in the Synthesis of Biphenyls

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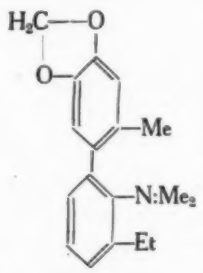
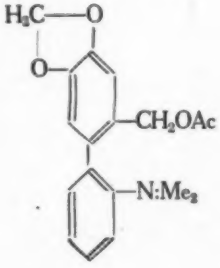
By application of the Ullmann reaction 2-methyl-4, 5-methylenedioxy-2′-nitrobiphenyl, 2, 3′-dimethyl-4, 5-methylenedioxy-2′-nitrobiphenyl, and 2-acetoxymethyl-2′ -dimethylamino-4, 5-methylenedioxybiphenyl have been synthesised.

With a view to studying the scope of the Ullmann reaction, syntheses of 3′-ethyl-2′-dimethylamino-2-methyl-4, 5-methylenedioxybiphenyl (I) and 2-acetoxymethyl-4, 5-methylenedioxy-2′-dimethylaminobiphenyl (II) have been investigated. The former biphenyl derivative was isolated by the Emde degradation of lycorine (Taylor *et al.*, *Chem. & Ind.*, 1954, 929), whereas compound (II) was believed to be one of the degradation products obtained from the alkaloid tazettine by a Hofmann degradation (Weisner and Valenta, *ibid.*, 1956, R. 36).




(I)




(II)

Synthesis of the biphenyl derivative (I) by application of the Ullmann reaction between 2-iodo-4, 5-methylenedioxytoluene (III) and 3-bromo-2-nitro-1-ethylbenzene (Elson *et al.*, *J. Chem. Soc.*, 1929, 2741) failed to provide the desired biphenyl. Model compounds, *e.g.*, 2-methyl-4, 5-methylenedioxy-2′-nitrobiphenyl and 2, 3′-dimethyl-4, 5-methylenedioxy-2′-nitrobiphenyl, could, however, be obtained by condensation of (III) with 2-nitro-1-bromobenzene and 3-bromo-2-nitrotoluene respectively under conditions of the Ullmann reaction.

The starting material for the preparation of compound (III) was the known 3, 4-methylenedioxytoluene, which was iodinated in ethanolic solution in presence of yellow mercuric oxide to yield 2-iodo-4, 5-methylenedioxytoluene. The position of iodine in (III) was established by oxidising it with potassium permanganate to 2-iodo-4, 5-methylenedioxybenzoic acid. The latter compound was also synthesised by another route, starting with the known 4, 5-methylenedioxy-2-nitrotoluene (Foulds and Robinson, *J. Chem. Soc.*, 1905, **105**, 1966), which on reduction and diazotisation gave 2-iodo-4, 5-methylenedioxytoluene. The latter being an oil had to be oxidised to the corresponding benzoic acid for purposes of comparison.

For the synthesis of compound (II), 6-bromopiperonal (Parijs, *Rec. trav. chim.*, 1930, **49,** 27; *Chem. Abs.*, 1929, **23,** 4204) was allowed to react with 2-bromo-1-nitrobenzene in presence of copper powder to form 2-formyl-4, 5-methylenedioxy-2′-nitrobiphenyl. The latter was reduced with sodium borohydride, when 2-hydroxymethyl-4, 5-methylenedioxy-2′-nitrobiphenyl (IV) resulted. On hydrogenation in presence of Raney nickel, 2′-amino-2-hydroxymethyl-4, 5-methylenedioxybiphenyl was obtained. Methylation of the latter and treatment with acetic anhydride afforded compound (II), m.p. 125-26°. In another experiment, (IV) was acetylated and the crude acetyl derivative was directly hydrogenated to afford 2-acetoxymethyl-2′-amino-4, 5-methylenedioxybiphenyl, isolated as an oil. This on methylation also gave (II), as indicated by mixed m.p.

## EXPERIMENTAL

3, 4-*Methylenedioxytoluene.*—To a suspension of $LiAlH_4$ (3.4 g.) in dry ether (120 c.c.) was added dropwise with stirring a solution of piperonyl chloride (5 g.) (Decker and Koch, *Ber.*, 1905, **38,** 174) in dry ether (30 c.c.). After stirring for 3 hours and gentle refluxing of ether, the excess reducing agent was decomposed with cold 10% $H_2SO_4$. On distillation of ether, an oil of b.p. 48-50°/2 mm was obtained; yield 2.5 g. (Ashkinazi and Rabinovitch, *J. Appl. Chem., U.S.S.R.*, 1937, **10,** 131).

2-*Iodo*-4, 5-*methylenedioxytoluene.*—A solution of 4, 5-methylenedioxytoluene (18.4 g.) in ethanol (50 c.c.) was treated alternately in small lots, with stirring, with finely powdered iodine (30.4 g.) and yellow mercuric oxide (16.5 g.) in course of an hour. The solution was filtered and the residue was washed with hot ethanol. The concentrated filtrate was taken up in ether and washed successively with 20% sodium thiosulphate, 10% NaOH solution, and water. After drying over anhydrous sodium sulphate it distilled at 108-10°/2 mm as a yellow oil; yield 12.0 g. (Found: I, 48.8. $C_8H_7O_2I$ requires I, 48.5%). It was obtained through another way (*vide infra*).

2-*Iodo*-4, 5-*methylenedioxybenzoic Acid.*—The preceding compound (1.0 g.) was added to a mixture of potassium permanganate (5.0 g.) and magnesium sulphate (2.0 g.) in water (60 c.c.). The solution was refluxed for 12 hours and then a current of sulphur dioxide was passed into it, when a solid separated out. It was crystallised twice from dilute methanol in white needles, m.p. 38-39°. (Found: I, 43.8. $C_8H_5O_4I$ requires I, 43.48%).

2-*Amino*-4, 5-*methylenedioxytoluene.*—4: 5-methylenedioxy-2-nitrotoluene (1.0 g.), dissolved in ethanol (25 c.c.), was hydrogenated in presence of Raney nickel for 4 hours. To the concentrated solution HCl (conc.) was added, when hydrochloride of 2-amino-4, 5-methylenedioxytoluene separated out. It was crystallised in fine white needles from methanol-ethyl acetate, m.p. 221-22°. (Found: N, 7.6. $C_8H_{10}O_2NCl$ requires N, 7.5%). The free amino compound was not very stable and after two crystallisations from methanol had m.p. 94-96°.

The amino-toluene was diazotised to-2-*iodo*-4: 5-*methylenedioxytoluene* in the following way: The hydrochloride of 2-amino-4, 5-methylenedioxytoluene (1.0 g.) in $H_2SO_4$ (conc., 1.6 c.c.) and crushed ice (8.5 g.) was treated below 0° with a solution of sodium nitrite (1.0 g.) in water (4.0 c.c.). The diazotised solution was then added to a solution of potassium iodide (1.0 g.) in water (2.0 c.c.), previously warmed to about 40°. The solution was extracted with ether, washed with a little HCl and water, and dried over anhydrous sodium sulphate. Distillation of ether furnished 2-iodo-4, 5-methylenedioxytoluene as an oil. It was oxidised as before to 2-iodo-4, 5-methylenedioxybenzoic acid, confirmed by mixed m.p. with the acid obtained before.

*2-Methyl-4, 5-methylenedioxy-2-nitrobiphenyl.*—A mixture of 2-iodo-4, 5-methylenedioxytoluene (2.2 g.) and 2-bromo-1-nitrotoluene (1.01 g.) (Ullmann, *Ber.*, 1896, **29B,** 1880) was heated to 170° and copper powder (2.2 g.) was added in small lots with stirring during 10 minutes; the mixture was kept at 168-70° for 10 minutes and then its temperature was raised to 225-30° and maintained there for 50 minutes. The mixture after being cooled was extracted with hot ethanol (125 c.c.), charcoaled, and the solvent removed by distillation. The residue was crystallised from ligroin (b.p. 100-120°) and finally sublimed at 120-22°/2 mm to furnish triangular plates, m.p. 134-35°, yield 0.95 g. (Found : C, 65.2 ; H, 4.3. $C_{14}H_{11}O_4N$ requires C, 65.3 ; H, 4.28%).

*3-Bromo-2-nitrotoluene* was prepared by a method analogous to that described for the preparation of 3-chloro-2-nitrotoluene (Elson *et al., loc. cit.*). The structure of the bromo compound was confirmed by its oxidation to the known 3-bromo-2-nitrobenzoic acid (Holleman, *Rec. trav. chim.*, 1901, **20,** 215).

*2, 3'-Dimethyl-4, 5-methylenedioxy-2'-nitrobiphenyl* was prepared from 2-iodo-4, 5-methylenedioxytoluene (1.98 g.) and 3-bromo-2-nitrotoluene (0.99 g.) with copper powder (2.2 g.) in the same way as described in the case of 2-methyl-4, 5-methylenedioxy-2'-nitrobiphenyl (*vide supra*) at 168°. It was crystallised from petroleum ether, m.p. 127-28°, yield 0.63 g. (Found : C, 66.6 ; H, 4.9. $C_{15}H_{13}O_4N$ requires C, 66.4 ; H, 4.8%).

*2-Formyl-4, 5-methylenedioxy-2-nitrobiphenyl.*—To a mixture of 6-bromopiperonal (6.06 g.) and 2-bromo-1-nitrobenzene (3.08 g.) was added copper bronze (7.0 g.) with stirring in course of 10 minutes, keeping the temperature at 175-85°. The temperature of the reaction mixture was gradually raised to about 240-45° and maintained there for 1 hour. The hard mass was extracted with a mixture of ethanol-acetone (2 : 1). The solution was charcoaled and the solvent distilled. The pasty mass obtained was boiled with rectified spirit (30 c.c.). The solid separating was filtered and sublimed at 200-10°/3 mm, and finally crystallised from ethyl acetate in brownish plates, m.p. 227-28°, yield 7.50 mg. (Found : C, 62.3 ; H, 3.4. $C_{14}H_9O_5N$ requires C, 61.98 ; H, 3.32%).

*2-Hydroxymethyl-4, 5-methylenedioxy-2'-nitrobiphenyl.*—To the preceding compound (0.5 g.) in methanol (15 c.c.) was added sodium borohydride (0.25 g.) ; the reaction mixture was refluxed for 2 hours. On cooling, acetic acid (2 c.c.) was added to decompose the excess of sodium borohydride. The concentrated solution was diluted with water, when a brown solid separated out. It was crystallised from methanol, m.p. 168-69°, yield 0.35 mg. (Found : N, 5.3. $C_{14}H_{11}O_5N$ requires N, 5.0%).

*2'-Amino-2-hydroxymethyl-4, 5-methylenedioxybiphenyl.*—A suspension of the above 2'-nitrobiphenyl derivative (100 mg.) in ethanol (30 c.c.) was reduced with Raney nickel (10 c.c. suspension) for 4 hours. The filtered solution was concentrated and then diluted with water to obtain the amino compound. It was crystallised from dilute methanol, m.p. 151-52°. (Found : C, 68.8 ; H, 5.8 ; N, 6.1. $C_{14}H_{13}O_3N$ requires C, 69.1 ; H, 5.4 ; N, 5.8%).

The same compound was also obtained by hydrogenation of 2-formyl-4, 5-methylenedioxy-2'-nitrobiphenyl in presence of Raney nickel.

*2-Acetoxymethyl-2'-dimethylamino-4, 5-methylenedioxybiphenyl.*—To the above aminobiphenyl (188 mg.) were added alternately and with stirring dimethyl sulphate (228 mg.) and 30% NaOH solution (0.25 c.c.) during 5 minutes. After further addition of the alkali (0.1 c.c.) the mixture was extracted with ether ; the ether solution was washed with 2-3 c.c. portions of water. After drying and distilling ether, a pasty mass was obtained. It was heated with acetic anhydride (1.5 c.c.) on a water bath for 5 minutes and the latter was removed under vacuum. The residue

was taken up in ether and the ether solution extracted with 2*N*-HCl (15 c.c.). The acid layer was separated and neutralised with 2*N*-NaOH to *p*H 8.0. The alkaline solution was extracted with ether and the ether solution was washed with water. Distillation of the ether gave a pale yellow solid. It was crystallised from petroleum ether (b.p. 40-60°), m.p. 125-26°. (Found : C, 68.6 ; H, 6.0 ; N, 4.8. $C_{18}H_{19}O_4N$ requires C, 68.99 ; H, 6.4 ; N, 4.47%).

In another experiment 2-hydroxymethyl-4, 5-methylenedioxy-2′-nitrobiphenyl was acetylated with acetic anhydride (0.7 c.c.) (containing a drop of pyridine) at 100° for 30 minutes. The resulting mixture was poured into water, when a brownish semi-solid was obtained. It did not solidify even after keeping in a refrigerator for 3 days. It was extracted with ether and the ether solution was washed successively with bicarbonate, HCl, and water. Removal of the solvent afforded 80 mg. of a dark oil. It was directly hydrogenated in ethanolic solution in presence of Raney nickel, when a brownish oil resulted. It was methylated, as described above, when a compound melting at 125-26° and identical with 2-acetoxymethyl-2′-dimethylamino-4, 5-methylenedioxybiphenyl was obtained (mixed m.p.).

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# Substituted Phenylhydrazines and their Derivatives

**Shiam Sunder Joshi and Daleep Singh Deorha**

Preparation of 2-chloro-5-bromo-, 2,5-dichloro-4-bromo-, 4-iodo-2-nitro-, and 4,6-dinitro-2-methyl-phenylhydrazines and their hydrazones with some carbonyl compounds are described.

In connection with some other work in this laboratory, a few phenylhydrazines and their condensation products with some carbonyl compounds were prepared by well known methods (Joshi and Deorha, this *Journal*, 1957, **34,** 14; 1951, **28,** 34). Similar compounds are reported in this communication.

## EXPERIMENTAL

*2-Chloro-5-bromophenylhydrazine.*—2-Chloro-5-bromoaniline (10.3 g.), suspended in HCl (conc., 50 c.c.), was diazotised by sodium nitrite (3.8 g.), dissolved in water (6 c.c.), at about 0°. The reaction product on treatment with a solution of stannous chloride (12 g.) in HCl (conc., 25 c.c.) separated as a crystalline precipitate of the hydrochloride of the corresponding base. It was washed with a saturated solution of sodium chloride and recrystallised from boiling HCl (dil.)

The base was obtained by adding an excess of NaOH solution to an aqueous solution of the hydrochloride, extracting with ether, and then removing the solvent.

2, 5-*Dichloro-4-bromophenylhydrazine* was similarly obtained from 2, 5-dichloro-4-bromoaniline.

4-*Iodo-2-nitrophenylhydrazine* was obtained from 4-iodo-2-nitroaniline by the method adopted for the preparation of 2-iodo-4-nitrophenylhydrazine (this *Journal*, 1957, **34,** 14).

4, 6-*Dinitro-2-methylphenylhydrazine* was prepared by the method already described (*ibid.*, 1951, **28,** 34). Characteristics of the phenylhydrazines, prepared as above, are shown in Table I.

TABLE I

| Phenylhydrazine. | Yield. | M.P. | Colour. | Formula. | % Nitrogen. Found. | Calc. |
|---|---|---|---|---|---|---|
| 2-Chloro-5-bromo- | 69% | 98° | Colorless | $C_6H_5N_2ClBr$ | 12.77 | 12.64 |
| 2, 5-Dichloro-4-bromo- | 70 | 107° | Do | $C_6H_3N_2Cl_2Br$ | 11.11 | 10.93 |
| 4-Iodo-2-nitro- | 75 | 123° | Red | $C_6H_6O_2N_3I$ | 14.96 | 15.05 |
| 4, 6-Dinitro-2-methyl- | 72 | 170° | Yellow | $C_7H_6O_4N_4$ | 26.38 | 26.41 |

Characteristics of the phenylhydrazones, prepared by heating equimolecular quantities of the substituted phenylhydrazines and the carbonyl compounds in ethanol, are shown in Tables II and III.

TABLE II

4-Iodo-2-nitro-2-methylphenylhydrazone.

| Carbonyl compounds. | M.P. | Colour | Formula. | %Iodine. Found. | %Iodine. Calc. |
|---|---|---|---|---|---|
| Formaldehyde | 137° | Orange | $C_7H_6O_2N_3I$ | 43.52 | 43.64 |
| Acetaldehyde | 160° | Do | $C_8H_8O_2N_3I$ | 41.78 | 41.64 |
| Benzaldehyde | 213° | Red | $C_{13}H_{10}O_2N_3I$ | 34.49 | 34.60 |
| Salicylaldehyde | 267° | Dark red | $C_{13}H_{10}O_3N_3I$ | 33.31 | 33.16 |
| Vanillin | 210° | Brown | $C_{14}H_{12}O_4N_3I$ | 30.82 | 30.75 |
| Cinnamic aldehyde | 225° | Red | $C_{15}H_{12}O_2N_3I$ | 32.11 | 32.24 |
| Anisaldehyde | 195° | Brown | $C_{14}H_{12}O_3N_3I$ | 32.13 | 31.99 |
| Acetone | 116° | Orange | $C_9H_{10}O_2N_3I$ | 40.14 | 39.81 |
| Methylethyl ketone | 105° | Orange-red | $C_{10}H_{12}O_2N_3I$ | 38.39 | 38.15 |
| Acetophenone | 156° | Red | $C_{14}H_{12}O_2N_3I$ | 33.21 | 33.33 |
| *p*-Methylacetophenone | 172° | Do | $C_{15}H_{14}O_2N_3I$ | 32.31 | 32.15 |

4, 6-Dinitro-2-methylphenylhydrazone.

| M.P. | Colour | Formula. | % Nitrogen Found. | % Nitrogen Calc. |
|---|---|---|---|---|
| 140° | Yellow | $C_8H_8O_4N_4$ | 25.12 | 25.0 |
| 126° | Do | $C_9H_{10}O_4N_4$ | 23.48 | 23.52 |
| 196° | Vermillion | $C_{14}H_{12}O_4N_4$ | 18.72 | 18.66 |
| 226° | Deep red | $C_{14}H_{12}O_5N_4$ | 17.88 | 17.72 |
| 240° | Red | $C_{15}H_{14}O_6N_4$ | 16.31 | 16.18 |
| 188° | Deep red | $C_{16}H_{14}O_4N_4$ | 17.27 | 17.18 |
| 182° | Chocolate-brown | $C_{15}H_{14}O_5N_4$ | 16.78 | 16.96 |
| 128° | Yellow | $C_{10}H_{12}O_4N_4$ | 22.28 | 22.22 |
| 104° | Do | $C_{11}H_{14}O_4N_4$ | 21.12 | 21.05 |
| 178° | Red | $C_{15}H_{14}O_4N_4$ | 18.02 | 17.83 |
| 203° | Do | $C_{16}H_{16}O_4N_4$ | 17.14 | 17.07 |

TABLE III

2-Chloro-5-bromophenylhydrazone.

| Carbonyl compounds. | M.P. | Colour. | Formula. | %Nitrogen. Found. | %Nitrogen. Calc. |
|---|---|---|---|---|---|
| Benzaldehyde | 112° | Colorless | $C_{13}H_{10}N_2ClBr$ | 9.17 | 9.04 |
| Salicylaldehyde | 150° | Do | $C_{13}H_{10}ON_2ClBr$ | 8.48 | 8.60 |
| Vanillin | 140° | Do | $C_{14}H_{12}O_2N_2ClBr$ | 7.92 | 7.87 |
| Cinnamic aldehyde | 100° | Light yellow | $C_{15}H_{12}N_2ClBr$ | 8.12 | 8.34 |
| 2-Chloro-5-nitrobenzaldehyde | 228° | Yellow | $C_{13}H_8O_2N_3Cl_2Br$ | 10.88 | 10.79 |

2, 5-dicholoro-4-bromophenylhydrazone.

| M.P. | Colour. | Formula. | %Nitrogen. Found. | %Nitrogen. Calc. |
|---|---|---|---|---|
| 128° | Colorless | $C_{13}H_9N_2Cl_2Br$ | 8.24 | 8.13 |
| 172° | Do | $C_{13}H_9ON_2Cl_2Br$ | 7.86 | 7.77 |
| 156° | Do | $C_{14}H_{11}O_2N_2Cl_2Br$ | 7.33 | 7.17 |
| 185° | Light yellow | $C_{15}H_{11}N_2Cl_2Br$ | 8.42 | 7.56 |
| 235° | Yellow | $C_{13}H_7O_2N_3Cl_2Br$ | 10.02 | 9.91 |

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# Ultraviolet Absorption Spectra of Sulphones. Part IV.* Effect of *ortho*-Substituents

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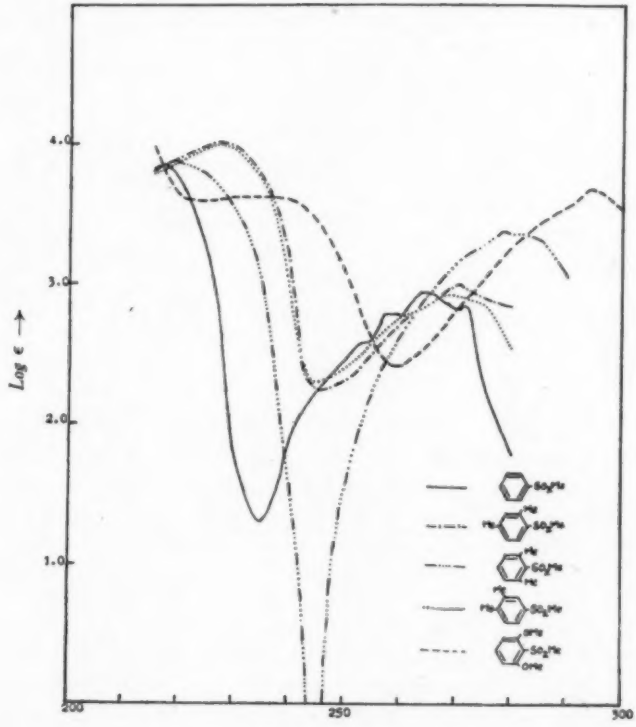
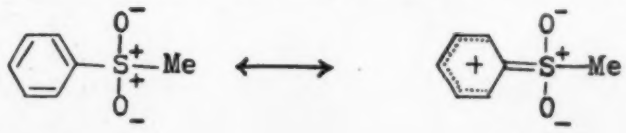
Several aryl methyl sulphones have been prepared and their ultraviolet absorption spectra recorded and analysed. Bulky *ortho*-substituents do not seem to cause any significant inhibition of conjugation of the sulphonyl group with the benzene nucleus in the electronically excited state. Ultraviolet absorption spectra of many substituted diaryl sulphones have also been recorded and analysed.

Methyl phenyl sulphone has a weak benzenoid band in the 250-270 mμ region and a strong band with maximum at 217 mμ (Fig. 1). The benzenoid band shows four absorption maxima

FIG. 1




due to vibrational transitions. The more intense band is presumably a K-band and it may be attributed to an electronically excited state receiving a contribution from structure (I).



(I)

* Part III : This *Journal*, 1958, **35**, 151.

The absorption spectra of a number of aryl methyl sulphones have been recorded in the present investigation with a view to studying the effect of *ortho*-substituents on the electronic interaction of the sulphonyl group with the benzene nucleus in the excited state. The data are recorded in Table I (see also Figs. 1-3).

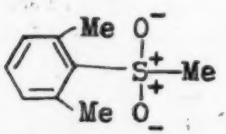
TABLE I

*UV absorption spectra of aryl methyl sulphones*, $ArSO_2Me$.

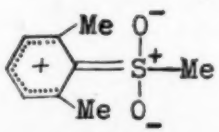
| Ar. | $\lambda_{max.}$ | $\epsilon_{max.}$ | Ar. | $\lambda_{max.}$ | $\epsilon_{max.}$ |
|---|---|---|---|---|---|
| Phenyl | 271mμ | 700 | 2,6-Dimethylphenyl | 278mμ | 2,400 |
| | 264 | 900 | | 219 | 7,400 |
| | 258 | 600 | | | |
| | 253 | 380 | 2,6-Dimethoxyphenyl | 294 | 4,700 |
| | 217 | 7,100 | | 232 | 4,100 |
| *o*-Tolyl | 277 | 1,450 | 2,4-Dimethylphenyl | 270 | 1,000 |
| | 270 | 1,700 | | 227 | 10,150 |
| | 219 | 7,200 | | | |
| | | | 3,4-Dimethylphenyl | 269 | 850 |
| *p*-Tolyl* | 273 | 460 | | 227 | 10,000 |
| | 267 | 540 | | | |
| | 262 | 560 | 2,5-Dimethylphenyl | 276 | 1,700 |
| | 257 | 450 | | 220 | 7,900 |
| | 225 | 11,750 | | | |
| | | | 2,5-Diethylphenyl | 283 | 1,800 |
| *o*-Butyl$^t$phenyl | 278 | 1,450 | | 276 | 1,900 |
| | 272 | 1,700 | | 221 | 9,000 |
| | 222 | 7,200 | | | |
| | | | 2,5-Dibutyl$^t$phenyl | 272 | 900 |
| Mesityl* | 285 | 1,800 | | 265 | 850 |
| | 280 | 1,600 | | 224 | 13,200 |
| | 277 | 1,700 | | | |
| | 230 | 8,900 | | | |

* Data from Fehnel and Carmack, *J. Amer. Chem. Soc.*, 1950, **72**, 1296.

While analysing the spectral data in relation to conjugation, we have to consider only the intense K-band, which is due to conjugation of the sulphonyl group with the benzene nucleus. It may be readily seen that a *p*-methyl group causes a bathochromic shift of the absorption maximum as well as an increase in intensity of the band while an *o*-methyl group does not seem to have any significant effect. The spectrum of *o*-butyl$^t$phenyl methyl sulphone is almost like that of methyl *o*-tolyl sulphone, the bulkiness of the *o*-butyl$^t$ group having no appreciable effect. Even in a compound like 2,6-dimethylphenyl methyl sulphone, the two *o*-methyl groups are not seen to inhibit conjugation of the sulphonyl group with the benzene nucleus. When a carbonyl or a nitro group conjugates with the benzene nucleus, coplanarity of the atoms (C and O or N, O and O) with the benzene nucleus is necessary if there is to be effective π-orbital interaction (cf. Braude and Sondheimer, *J. Chem. Soc.*, 1955, 3754; Wepster, *Rec. trav. chim.*, 1957, **76**, 335).




(II)



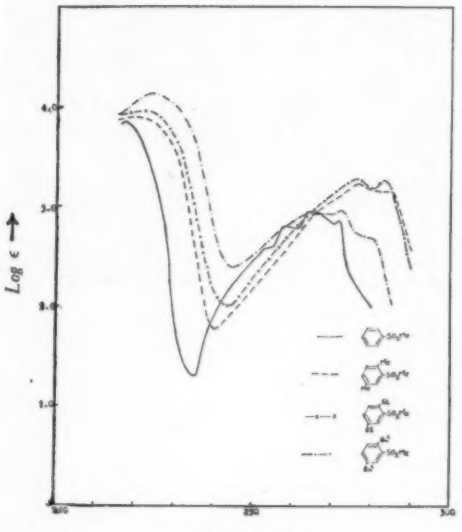

(III)

When conjugation with the sulphonyl group occurs, the situation is different. Sulphur can expand its valence shell by utilising its vacant *d*-orbitals. If we consider the ground state of

2,6-dimethylphenyl methyl sulphone, structure (II) may be assumed to contribute chiefly to it. The four valence bonds in (II) result from $3s3p^3$ hybridisation. The bonds may be taken as essentially tetrahedral. Structure (III) makes a significant contribution to the excited state. The four $\sigma$-bonds in it are still tetrahedral. The $\pi$-bond seems to be possible by the overlapping of the $2p$-orbital of carbon and the $3d$-orbital of sulphur. In that case planarity of the atoms in the sulphonyl group with the benzene nucleus is not necessary for conjugation (see also Fehnel and Carmack, *loc. cit.*). Thus the absence of steric inhibition of conjugation in the excited state of 2,6-dimetylphenyl methyl sulphone becomes clear.

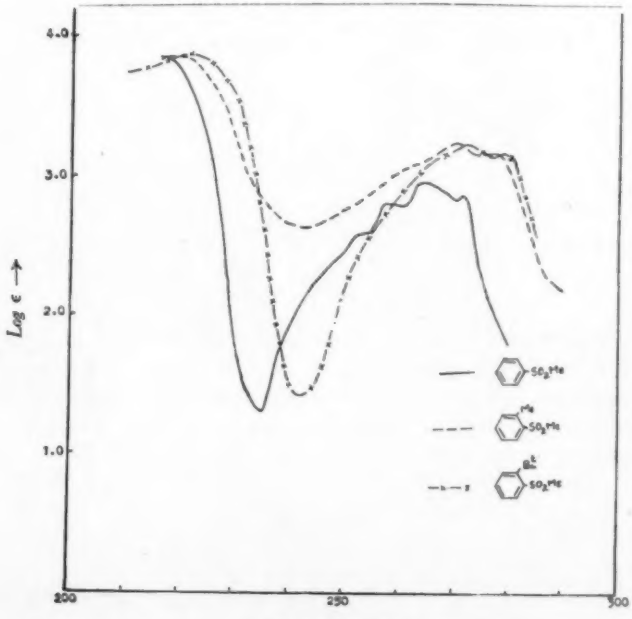
The absorption spectra of many diaryl sulphones were also taken in the present study with a view to examining polar and steric effects. The data are shown in Table II.

FIG. 2




*Wave length (mμ).*

FIG. 3




*Wave length (mμ).*

TABLE II

*UV absorption spectra of diaryl sulphones.*

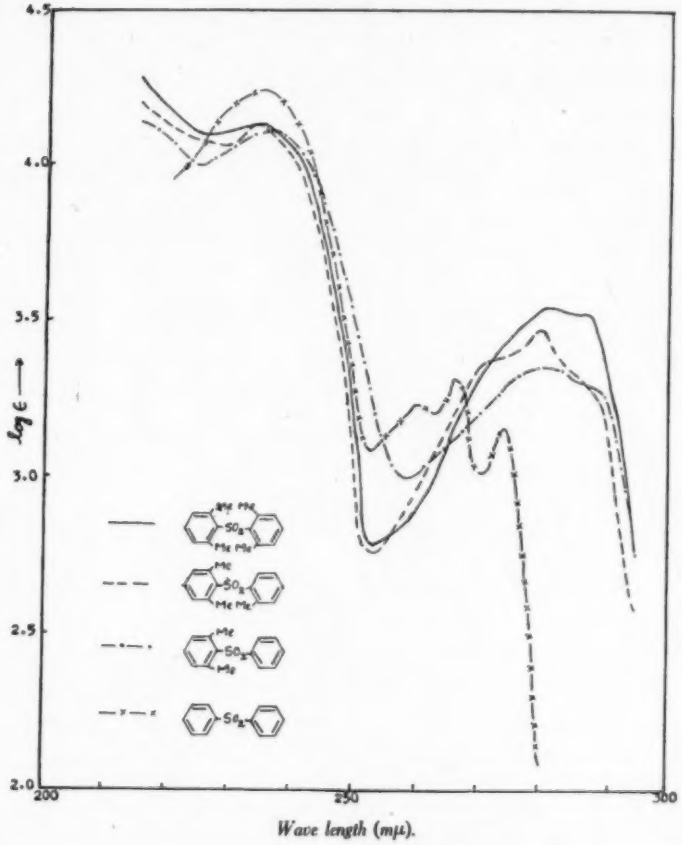
| Sulphone. | $\lambda_{max.}$ | $\epsilon_{max.}$ | Sulphone. | $\lambda_{max.}$ | $\epsilon_{max.}$ |
|---|---|---|---|---|---|
| Diphenyl (D) | 274mμ | 1,450 | 2-Methyl-4′-methoxy-D | 252mμ | 18,700 |
| | 266 | 2,100 | | | |
| | 260 | 1,800 | 2,2′-Dimethyl-4-methoxy-D | 253 | 18,000 |
| | 235 | 17,400 | | | |
| | | | 2-Methoxy-5,2′-dimethyl-D | 298 | 4,400 |
| * 2-Methyl-D | 266.5 | 2,000 | | 223 | 18,400 |
| | 273.5 | 2,200 | | | |
| | 234.0 | 14,100 | 2-Methoxy-4,2′-dimethyl-D | 289 | 4,900 |
| | | | | 240 | 12,900 |
| * 4-Methyl-D | 274 | 1,350 | | | |
| | 266 | 2,350 | 2-Methoxy-4-methyl-D | 291 | 5,600 |
| | 241 | 18,200 | | 241 | 14,700 |
| 2,6-Dimethyl-D | 280 | 2,300 | 2-Methoxy-4,4′-dimethyl-D | 290 | 5,000 |
| | 235 | 12,850 | | 244 | 16,400 |
| | | | | 226 | 16,700 |
| 2,6,2′-Trimethyl-D | 279 | 3,000 | | | |
| | 233 | 13,400 | 2-Methoxy-5-methyl-D | 298 | 4,300 |
| | | | | 221 | 20,700 |
| 2,6,2′,6′-Tetramethyl-D | 286 | 3,400 | | | |
| | 279 | 3,550 | 2-Methoxy-5,4′-dimethyl-D | 298 | 4,450 |
| | 234 | 13,600 | | 238 | 14,700 |
| | | | | 226 | 18,700 |
| 2-Methoxy-D | 290 | 4,600 | | | |
| | 235 | 12,000 | 2,4-Dimethoxy-D | 287 | 7,150 |
| | 219 | 16,400 | | 252 | 14,800 |
| 3-Methoxy-D | 290 | 3,100 | 2,6-Dimethoxy-D | 300 | 4,800 |
| | 275 | 2,400 | | 248 | 9,700 |
| | 224 | 18,100 | | | |
| | | | 2,6,2′,6′-Tetramethoxy-D | 293 | 7,700 |
| 4-Methoxy-D | 254 | 18,000 | | 252 | 15,100 |
| 2-Methyl-4-methoxy-D | 253 | 16,900 | | | |

* Data from Leandri *et al.*, *Gazzetta*, 1954, **84**, 73.

The K-band of diphenyl sulphone has maximum at 235 mμ. This band may be attributed to the conjugation of the sulphonyl group with the two benzene nuclei. It undergoes displacement towards longer wave length with increase in intensity when a methyl or a methoxyl group is present *para* to the sulphonyl group. This is in agreement with the view that in the case of *para*-disubstituted benzene derivatives, if the two groups enhance the tendency for electron transfer in the same direction, a bathochromic shift occurs. When a methyl group is present in the *para* position, the 235 mμ band is seen to shift to the 240-245 mμ region ; in the case of a *p*-methoxy sulphone the band shifts to the 250-255 mμ region.

The presence of one or more *o*-methyl groups does not significantly alter the absorption maximum, but there is a reduction in intensity (see Fig. 4).

FIG. 4

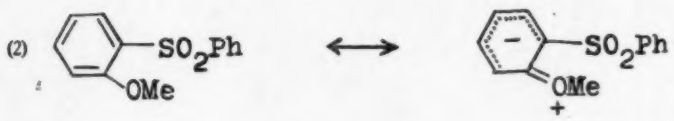



The presence of one *o*-methoxyl group does not alter the absorption maximum, but when more methoxyl groups are present in the *ortho* position a bathochromic shift occurs, there being reduction in the intensity of absorption in all cases. The *ortho* effects, observed in diaryl sulphones, are thus somewhat different from those observed in aryl methyl sulphones. An explanation was offered by Baliah and Ramakrishnan (this *Journal*, 1958, **35**, 151) for some of the *ortho* effects seen in diaryl sulphones.

(I)

Some of the spectral data recorded in Table II can be explained on the basis that the methoxyl or methyl group is forced out of the plane of the benzene ring when present *ortho* to a sulphonyl group. For example, in 2-methoxydiphenyl sulphone there seem to be two electronic excitations : (1) the methoxyl group being forced out of the plane of the benzene ring, $-SO_2-$ conjugates with

the benzene nuclei, (2) the phenylsulphonyl group being forced out of the plane of the benzene ring. -OMe conjugates with the benzene nucleus. 2-Methoxydiphenyl sulphone exhibits three absorption maxima ($\lambda_{max}$ 280, 273, 233 mμ ; $\epsilon_{max}$ 2500, 2700, 14500). The bands at 280 and 273 mμ may be ascribed to electronic excitation (2), described above (cf. the spectrum of anisole : $\lambda_{max}$ 278,271,222 mμ ; $\epsilon_{max}$ 1400, 2100, 7300). The band at 233 mμ may be ascribed to electronic excitation (1) since diphenyl sulphone absorbs maximally at 235 mμ.




## EXPERIMENTAL

*o-Butyl'thiophenol.*—Sulphuric acid (*d* 1.12, 120 c.c.) was added to *o*-butyl'aniline (Shoesmith and Mackie, *J. Chem. Soc.*, 1928, 2337 (10 g.) and the mixture was stirred well to ensure formation of finely divided amine sulphate. The contents of the flask were cooled to -12° in an ice-salt mixture. The amine sulphate was diazotised with a cold solution of sodium nitrite (10 g.) in water (20 c.c.). It was found necessary to maintain the temperature at -12° since the diazonium compound decomposed above -10°. The diazonium sulphate solution was then added to a solution of potassium ethyl xanthate (50 g.) and sodium carbonate (25 g.) in water (200 c.c.), kept at 70°. The mixture was heated on a water bath for 1 hour to complete the decomposition. The oil being settled was extracted with ether, washed with a 10% NaOH solution (20 c.c.) and then with water, and dried ($CaCl_2$).

After removal of the ether the xanthogenic ester was taken up in ethanol (95%, 200 c.c.) contained in a 1-litre r.b. flask, and refluxed. To the boiling solution were added potassium hydroxide pellets (40 g.) at such a rate that the hydrolysis did not become too vigorous. After the addition, the mixture was refluxed for 8 hours and as much of ethanol as possible was removed by distillation. The mixture was then acidified with $H_2SO_4$ (1:1, 50 c.c.), zinc dust (10 g.) was added, and distilled in steam until no more oily drops passed over. The distillate was extracted with ether and dried ($CaCl_2$). The thiophenol, that remained after removal of the ether, boiled at 84-86°/10 mm, yield 2.6 g. It has a highly unpleasant characteristic odour. ( Found : C, 72.3 ; H, 8.55. $C_{10}H_{14}S$ requires C, 72.2 ; H, 8.5%).

*o-Butyl'phenylmethyl Sulphide.*—*o*-Butyl'thiophenol was methylated using methyl iodide in absolute ethanol containing sodium ethoxide. The mixture was left overnight, refluxed for 2 hours on a water bath, and poured into water. The oil separating was extracted with ether ; the ether extract was first washed with a 10% NaOH solution (10 c.c.) and then with water, and dried ($CaCl_2$). After evaporation of the ether, the sulphide (2 g.) distilled at 118-20°/7 mm. (Found : C, 73.45 ; H, 9.4. $C_{11}H_{16}S$ requires C, 73.3 ; H, 8.9%).

*o-Butyl'phenyl Methyl Sulphone.*—The foregoing sulphide in acetic acid was treated with a solution of $KMnO_4$ and left overnight. The excess of $KMnO_4$ and the precipitated $MnO_2$ were reduced with $SO_2$ and the clear solution was evaporated to dryness on a water bath. The residue was triturated thrice with acetone and the acetone was removed from the combined extracts. The separated oil soon solidified, m.p. 69-70° (dilute ethanol). (Found : C, 62.4 ; H, 7.5. $C_{11}H_{16}O_2S$ requires C, 62.2 ; H, 7.6%).

2,6-*Dimethylphenyl Methyl Sulphone.*—2, 6-Dimethlthiophenol (Kazimi *et al.*, *J. Amer. Chem. Soc.*, 1955, **77**, 2479) was methylated and the methyl sulphide was oxidised with $KMnO_4$ in acetic acid. The sulphone was obtained in 90% yield, m.p. 93-94°. Bolssens *et al.* (*Rec. trav chim.*, 1954, **73**, 836) report m.p. 94.5-95°.

2,5-*Dimethylphenyl Methyl Sulphone.*—2,5-Dimethylbenzenesulphonyl chloride (Huntress and Autenrieth, *J. Amer. Chem. Soc.*, 1941, **63**, 3446) was reduced with zinc dust and water to afford sodium 2,5-dimethylbenzenesulphinate. The sulphinate (20 g.) was methylated with methyl iodide (16 g.) in absolute ethanol (75 c.c.). The yield of the sulphone was 6 g., m.p. 39-40° (dilute ethanol). (Found : C, 58.8 ; H, 6.5. $C_9H_{12}O_2S$ requires C, 58.7 ; H, 6.6%).

2,4-*Dimethylphenyl methyl sulphone* was prepared from 2,4-dimethylbenzenesulphonyl chloride as in the previous case. After recrystallisation from dilute ethanol it melted at 55°. Tröger and Budde (*J. prakt. Chem.*, 1902, **66**, 149) report the same m.p.

3,4-*Dimethylphenyl methyl sulphone* was also obtained from the corresponding sulphonyl chloride, It melted at 72-73° (dilute ethanol). (Found : C, 58.8 ; H, 6.3. $C_9H_{12}O_2S$ requires C, 58.7 ; H, 6.6%).

2,5-*Dibutylphenyl Methyl Sulphone.*—Here again the starting material was the corresponding sulphonyl chloride. The sulphonyl chloride underwent reduction only after refluxing for 8 hours with zinc dust and water. The sulphinate on methylating with methyl iodide yielded the sulphone, m.p. 70-71° (ethanol-water). (Found : C, 67.2 ; H, 8.9. $C_{15}H_{24}O_2S$ requires C, 67.1 ; H, 9.0%).

2,5-*Diethylphenyl Methyl Sulphone.*—2,5-Diethylbenzenesulphonyl chloride, obtained by the chlorosulphonylation of *p*-diethylbenzene (Auwers, *Annalen*, 1919, **419**, 115), was reduced to the corresponding sodium sulphinate and methylated with methyl iodide. The sulphone boiled at 146-48°/6 mm. (Found : C, 62.1 ; H, 7.5. $C_{11}H_{16}O_2S$ requires C, 62.15 ; H, 7.6%).

2,6-*Dimethoxythiophenol.*—2,6-Dimethoxyaniline (Kauffmann and Franck, *Ber.*, 1907, **40**, 4006) (15.3 g.) was diazotised and the diazonium solution was added to a solution of potassium ethyl xanthate (30 g.) and sodiun carbonate (20 g.) in water (60 c.c.), maintained at 70°. The mixture was heated on a water bath for 2 hours. The xanthogenic ester was taken up in ether, washed with a 10% solution of NaOH (20 c.c.) and then with water, and dried ($CaCl_2$). The ether was removed and the xanthogenic ester was hydrolysed. The thiophenol was removed by steam distillation. After recrystallising from ethanol, the thiophenol (5.3 g.) melted at 85-86°. (Found : C, 56,9 ; H, 6.0. $C_8H_{10}O_2S$ requires C, 56.45 ; H, 5.9%).

2,6-*Dimethoxyphenylmethyl Sulphide.*—Methylation of the foregoing thiophenol with methyl iodide in absolute ethanol solution containing sodium ethoxide furnished this sulphide in almost quantitative yield. On recrystallisation from ethanol it melted at 79-81°. (Found : C, 58.8 ; H, 6.7. $C_9H_{12}O_2S$ requires C, 58.7 ; H, 6.6%).

2,6-*Dimethoxyphenyl methyl sulphone* was obtained by oxidising the above sulphide with hydrogen peroxide. It melted at 139-40° (water). (Found : C, 49.5 ; H, 5.3. $C_9H_{12}O_4S$ requires C, 50.0 ; H, 5.6%).

2,2', 6,6'-*Tetramethoxydiphenyl Sulphide.*—To a solution of 2,6-dimethoxythiophenol (2.5 g.) in absolute ethanol (20 c.c.) sodium (0.4 g.) was added and the ethanol was distilled off. 2,6-Dimethoxyiodobenzene (Kauffmann and Franck, *loc. cit.*) (4 g.) and copper powder (0.2 g.) were added to the dry sodium salt of the thiophenol and the mixture was heated in an oil bath for 4 hours at 200-20°. After cooling, the mixture was triturated thrice with ethanol. $H_2SO_4$ (1:1 ; 20 c.c.) and zinc dust (5 g.) were added to the extract and the mixture was distilled in steam to remove the

unchanged thiophenol and the iodo compound. The solid in the flask was filtered and triturated several times with ethanol. Distillation of ethanol gave the sulphide (2.8 g.) which, after recrystallising eight times from acetic acid and finally from ethanol, melted at 152-54°. (Found : C, 62.8 ; H, 5.9. $C_{16}H_{18}O_4S$ requires C, 62.7 ; H, 5.9%).

2,2', 6,6'-*Tetramethoxydiphenyl Sulphone.*—The foregoing sulphide (0.05 g.) in acetone was oxidised with hydrogen peroxide. The yield of the sulphone was 0.02 g. It was recrystallised from water, m.p. 175-76° (decomp.). (Found : C, 56.7 ; H, 5.3. $C_{16}H_{18}O_6S$ requires C, 56.8 ; H, 5.4%).

2,2', 6,6'-*Tetramethyldiphenyl Sulphide.*—2,6-Dimethylthiophenol (0.1 *M*) and 2,6-dimethyliodobenzene (Kohlrausch and Pongratz, *Monatsh.*, 1934, **64,** 369) (0.1 *M*) were added to a solution of sodium ethoxide (0.1 *M*) in absolute ethanol and the excess ethanol was removed. The mixture was heated at 250-60° for 4 hours in presence of copper powder. On working up the product in the usual way, the sulphide was obtained in 60% yield. Repeated recrystallisation from ethanol gave colorless prisms, m.p. 79-80°. (Found : C, 79.2 ; H, 7.4. $C_{16}H_{18}S$ requires C, 79. 3 ; H, 7.5%).

2,2',6,6'-*Tetramethyldiphenyl Sulphone.*—The foregoing sulphide on oxidation with $KMnO_4$ afforded the sulphone in 95% yield. It was recrystallised from ethanol, m.p. 129-30°. (Found : C, 70.4 ; H, 6.7. $C_{16}H_{18}O_2S$ requires C, 70.0 ; H, 6.6%).

2,2',6*Trimethyldiphenyl sulphide* was obtained from 2,6-dimethylthiophenol and *o*-iodotoluene in 60% yield, m.p. 89-90° (ethanol). (Found : C, 78.6 ; H, 7.05. $C_{15}H_{16}S$ requires C, 78.9 ; H, 7.1%).

2,2'6,-*Trimethyldiphenyl Sulphone.*—Oxidation of the above sulphide with $KMnO_4$ yielded the sulphone, m.p. 104-105° (ethanol). (Found : C, 69.5 ; H, 6.3. $C_{15}H_{16}O_2S$ requires C, 69.2 ; H, 6.2%).

2,6-*Dimethyldiphenyl sulphide* was obtained from 2,6-dimethylthiophenol and iodobenzene. The compound boiled at 142°/10 mm. Truce and Ray (*J. Amer. Chem. Soc.*, 1959, **81,** 481) report b.p. 112-22°/1 mm.

2,6-*Dimethyldiphenyl Sulphone.*—Oxidation of the foregoing sulphide with $KMnO_4$ afforded this sulphone in 85% yield, m.p. 101-102° (ethanol). Truce and Ray (*loc. cit.*) report the same m.p.

*Ultraviolet Absorption Spectra.*—The ultraviolet absorption spectra were determined with a Beckman quartz spectrophotometer, model DU. The solvent used was 95% ethanol.

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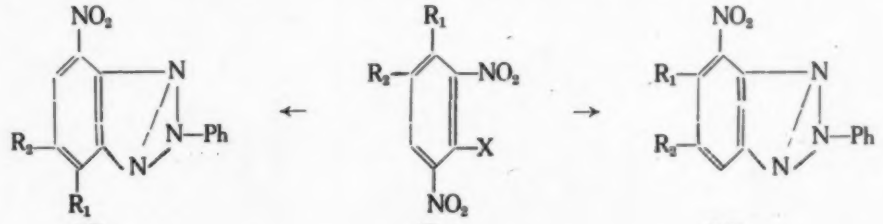
# Behaviour of Chloronitrobenzenes with Hydrazine and Hydrazine Derivatives. Part XII. *2-Phenyl-1,2,3-benzotriazoles and their 1-Oxides

**Daleep Singh Deorha and Shiam Sunder Joshi**

A few 2-phenyl-1,2,3-benzotriazoles and their 1-oxides have been obtained by interaction of phenylhydrazines and halogenonitrobenzenes. Where formation of more than one triazole is possible, only one triazole has been isolated. Structures to such compounds have been assigned.

In this communication are described a few characteristics of several 2-phenyl-1, 2, 3-benzotriazoles and their 1-oxides (Tables I and II), obtained by condensing phenylhydrazines with halogenonitrobenzenes. Of these (I a), (I b), and (I c) can possibly yield two 2-phenyl-1, 2, 3-benzotriazoles, though only one has been isolated in each case. The structure to the products can be assigned by a procedure reported by one of us (Deorha, Agra University Ph.D. thesis, 1953) and subsequently by Joshi and Gupta (this *Journal*, 1958, **35,** 681). Thus in case of the product (IIa or IIIa) from 4-chloro-1-bromo-2, 6-dinitro-3-methylbenzene, when the nitro group was substituted by a chlorine atom, the dichloro-2-phenyl-1, 2, 3-benzotriazole obtained was found to be identical with 4, 6-dichloro-7-methyl-2-phenyl-1, 2, 3-benzotriazole, formed similarly from 4-chloro-6-nitro-7-methyl-2-phenyl-1, 2, 3-benzotriazole. The structure of the latter follows from its synthesis from 2-chloro-1-bromo-4, 6-dinitro-5-methylbenzene and phenylhydrazine. Therefore the triazole from (I a) must also have the methyl group in position 7 and must be (II a).




I a: $R_1$ = Me; $R_2$ = Cl; X = Br.
I b $R_1$ = Me; $R_2$ = Br; X = Br.
I c: $R_1$ = Me; $R_2$ = $NO_2$; X = Cl.
I d: $R_1$ = Cl; $R_2$ = Cl; X = Cl.
I e: $R_1$ = Br; $R_2$ = Cl; X = Cl.

By condensation of (I d) with phenylhydrazine Walter (Dissertation, Freiburg, B, 1889, S28) obtained a 2-phenyl-1, 2, 3-benzotriazole to which he could not assign a definite structure as three isomeric compounds could probably result from the reaction. Identical products are obtained by heating (I d) and (I e) with phenylhydrazine in ethanolic solutions; both of them must therefore be 4: 7-dichloro-6-nitro-2-phenyl-1, 2, 3-benzotriazole.

*Part XI: This *Journal*, 1960, **37,** 690.

TABLE I

*2-Phenyl-1, 2, 3-benzotriazoles.*

| Halogenonitrobenzene. | 2-Phenylbenzotriazole. | Yield. | M.P. | Colour. | Formula. | Found. | Calc. |
|---|---|---|---|---|---|---|---|
| 1-Bromo-4, 6-dinitro-3-methyl- | 6-Nitro-5-methyl- | 72% | 155° | Buff | $C_{13}H_{10}O_2N_4$ | N : 21.94% | 22.05% |
| 1, 2-Dibromo-4, 6-dinitro-5-methyl- | 4-Bromo-6-nitro-7-methyl- | 45 | 178° | Light yellow | $C_{13}H_9O_2N_4Br$ | Br : 23.88 | 24.02 |
| 2-Chloro-1-bromo-4, 6-dinitro-5-methyl- | 4-Chloro-6-nitro-7-methyl- | 53 | 155° | Buff | $C_{13}H_9O_2N_4Cl$ | Cl : 12.51 | 12.30 |
| 1, 4-Dibromo-2, 6-dinitro-3-methyl- | 6-Bromo-4-nitro-7-methyl- | 54 | 165° | Sepia | $C_{13}H_9O_2N_4Br$ | Br : 23.76 | 24.02 |
| 4-Chloro-1-bromo-2, 6-dinitro-3-methyl- | 6-Chloro-4-nitro-7-methyl- | 50 | 160° | Yellow | $C_{13}H_9O_2N_4Cl$ | Cl : 12.43 | 12.30 |
| 2-Chloro-1-bromo-4, 6-dinitro- | 4-Chloro-6-nitro- | 79 | 179° | Sepia | $C_{12}H_7O_2N_4Cl$ | Cl : 12.54 | 12.93 |
| 1-Chloro-3-bromo-4, 6-dinitro- | 5-Chloro-6-nitro- | 69 | 207° | Yellow | $C_{12}H_7O_2N_4Cl$ | Cl : 13.13 | 12.93 |
| 1, 2, 3-Tribromo-4, 6-dinitro- | 4, 5-Dibromo-6-nitro- | 80 | 206° | Cream | $C_{12}H_6O_2N_4Br_2$ | Br : 39.82 | 40.20 |
| 2-Chloro-1, 3-dibromo-4, 6-dinitro- | 4-Chloro-5-bromo-6-nitro- | 82 | 213° | Light buff | $C_{12}H_6O_2N_4ClBr$ | Cl + Br : 32.39 | 32.67 |
| 1, 2, 3-Trichloro-4, 6-dinitro- | 4, 5-Dichloro-6-nitro- | 84 | 198° | Buff | $C_{12}H_6O_2N_4Cl_2$ | Cl : 23.14 | 22.97 |
| 1, 2, 4-Trichloro-3, 5-dinitro- | 4, 7-Dichloro-6-nitro- | 69 | 166° | Sepia | $C_{12}H_6O_2N_4Cl_2$ | Cl : 22.86 | 22.97 |
| 1, 4-Dichloro-2-bromo-3, 5-dinitro- | 4, 7-Dichloro-6-nitro- | 68 | 166° | Sepia | $C_{12}H_6O_2N_4Cl_2$ | Cl : 22.78 | 22.97 |

TABLE II

*2-Phenyl-1, 2, 3-benzotriazole-1-oxides.*

| Halogenonitrobenzene. | 2-Phenylbenzotriazole-1-oxide. | Yield. | M.P. | Colour. | Formula. | Found. | Calc. |
|---|---|---|---|---|---|---|---|
| 4-Chloro-1-iodo-2, 6-dinitro- | 6-Chloro-4-nitro- | 70% | 204° | Golden yellow | $C_{12}H_7O_3N_4Cl$ | Cl : 11.81% | 12.22% |
| 1-Bromo-4, 6-dinitro-3-methyl- | 6-Nitro-5-methyl- | 73 | 190° | Do | $C_{13}H_{10}O_3N_4$ | N : 21.04 | 20.74 |
| 2-Chloro-1-bromo-4, 6-dinitro- | 4-Chloro-6-nitro- | 65 | 202° | Yellow | $C_{12}H_7O_3N_4Cl$ | Cl : 11.97 | 12.22 |
| 4-Bromo-1-iodo-2, 6-dinitro- | 6-Bromo-4-nitro- | 72 | 198° | Golden yellow | $C_{12}H_7O_3N_4Br$ | Br : 23.42 | 23.88 |
| 1-Chloro-3-bromo-4, 6-dinitro- | 5-Chloro-6-nitro- | 68 | 195° | Fawn | $C_{12}H_7O_3N_4Cl$ | Cl : 12.03 | 12.22 |
| 1, 2, 3-Tribromo-4, 6-dinitro- | 4, 5-dibromo-6-nitro- | 70 | 203° | Buff | $C_{12}H_6O_3N_4Br_2$ | Br : 38.98 | 38.64 |
| 2-Chloro-1, 3-dibromo-4, 6-dinitro- | 4-Chloro-5-bromo-6-nitro- | 72 | 212° | Fawn | $C_{12}H_6O_3N_4ClBr$ | Cl + Br : 31.54 | 31.25 |
| 1, 2, 3-Trichloro-4, 6-dinitro- | 4, 5-Dichloro-6-nitro- | 71 | 192° | Light buff | $C_{12}H_6O_3N_4Cl_2$ | Cl : 21.63 | 21.84 |
| 1, 2, 4-Trichloro-3, 5-dinitro- | 4, 7-Dichloro-6-nitro- | 68 | 178° | Light yellow | $C_{12}H_6O_3N_4Cl_2$ | Cl : 21.52 | 21.84 |
| 1, 4-Dichloro-2-bromo-3, 5-dinitro- | 4, 7-Dichloro-6-nitro- | 67 | 178° | Do | $C_{12}H_6O_3N_4Cl_2$ | Cl : 21.71 | 21.84 |
| 1-Chloro-2-bromo-4, 6-dinitro- | 4-Bromo-6-nitro- | 70 | 202° | Yellow | $C_{12}H_7O_3N_4Br$ | Br : 23.51 | 23.88 |
| 1-Chloro-2, 4, 6-trinitro-3-methyl- | 4, 6-Dinitro-7-methyl- | 69 | 201° | Dirty yellow | $C_{13}H_9O_5N_5$ | N : 22.39 | 22.22 |

## EXPERIMENTAL

*2-Phenyl-1, 2, 3-benzotriazoles and their 1-Oxides.*—The compounds, described in Tables I and II, were prepared by heating the halogenonitrobenzenes with phenylhydrazine (cf. Joshi and Gupta, *loc. cit.*).

*4,6-Dichloro-7-methyl-2-phenyl-1, 2, 3-benzotriazole.*—4-Chloro-6-amino-7-methyl-2-phenyl-1, 2, 3-benzotriazole, obtained by reduction of 4-chloro-6-nitro-7-methyl-2-phenyl-1, 2,3-benzotriazole, was crystallised from ethanol in colorless needles, m.p. 170°. (Found : Cl, 13.94. $C_{13}H_{11}N_4$ Cl requires Cl, 13.73%).

4, 6-Dichloro-7-methyl-2-phenyl-1, 2, 3-benzotriazole, obtained from the above compound by the replacement of amino group by a chlorine atom, was crystallised from benzene in colorless crystals, m.p. 148°. (Found : Cl, 25.23. $C_{13}H_9N_3Cl_2$ requires Cl, 25.24%).

Similarly 6-chloro-4-nitro-5 (or 7) -methyl-2-phenyl-1, 2, 3-benzotriazole gave 6-chloro-4-amino-5 (or 7)-methyl-2-phenyl-1, 2, 3-benzotriazole which was crystallised from ethanol in light yellow crystals, m.p. 180°. (Found : Cl, 13.82. $C_{13}H_{11}N_4Cl$ requires Cl, 13.73%) and then dichloro- 2-phenyl-1, 2, 3-benzotriazole, m.p. 148°, which was found to be identical with 4,6-dichloro- 7-methyl-2-phenyl-1, 2, 3-benzotriazole.

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# 1-Alkyl-substituted 2,4-Dithiobiurets and Related Thiurets: Interaction of Aliphatic Amines and Isopersulphocyanic Acid

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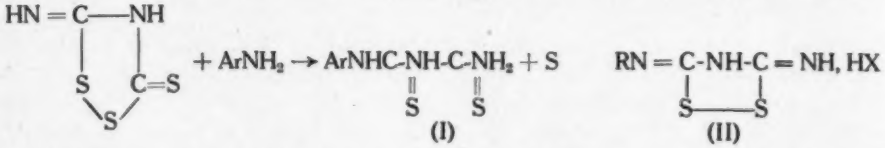
Preparation of a number of 1-alkyl-substituted 2, 4-dithiobiurets by the action of aliphatic amines on isopersulphocyanic acid has been described. Related thiurets have also been obtained by their oxidation.

1-Aryl-substituted 2, 4-dithiobiurets (I) are easily obtained by the action of aromatic amines on isopersulphocyanic acid (Glutz, *Annalen*, 1870, **154,** 44; Fromm *et al.*, *ibid.*, 1893, **275,** 34; 1908, **361,** 319; 1906, **348,** 167, 173; *Ber.*, 1895, **28,** 1099; Tursini, *Ber.*, 1884, **17,** 585, 586).



Alkyl analogues of the dithiobiurets, only a few of which are known (Hecht, *Ber.*, 1892, **25,** 753, 754), appear to have been obtained, however, by the action of hydrogen sulphide on the related *N*-alkyl-*N'*-cyanothiocarbamides (Wunderlich, *Ber.*, 1886, **19,** 449; Hecht, *loc. cit.*, p.753). This last group of compounds has not been sufficiently well characterised, and what is more, experience has shown that addition of hydrogen sulphide is not quite as easy to accomplish as hydrolysis. Consequently, the yields are poor and the method entails a heavy loss of expensive starting materials like alkyl isothiocyanates.

The interaction of aliphatic amines and isopersulphocyanic acid, which does not appear to have been studied hitherto, has therefore been investigated in the hope of extending it to the preparation of 1-alkyl-substituted 2, 4-dithiobiurets. The reaction is found, at ordinary temperatures, analogous to that with aromatic amines, and it affords 1-alkyl-substituted 2, 4-dithiobiurets in good yields. When the reaction was carried out at higher temperatures (water bath) sulphur, aminethiocyanate, $H_2S$, etc. were obtained instead of the expected dithiobiuret, which was undoubtedly formed as the primary product but later was decomposed.

Like the aromatic derivatives (Fromm *et al.*, *Ber.*, 1895, **28,** 1100; *Annalen*, 1893, **275,** 42; 1906, **348,** 161; 1907, **356,** 179; 1908, **361,** 320; 1912, **394,** 260, 265) 1-alkyl-substituted 2, 4-dithiobiurets are easily oxidised in an acidic medium to the related thiurets (II).

## EXPERIMENTAL

*Formation of 1-Alkyl-substituted 2, 4-Dithiobiurets.*—Isopersulphocyanic acid and a strong aqueous solution of the desired amine were mixed at ordinary temperature. The reaction mixture warmed on stirring; the persulphocyanic acid went gradually into solution, followed by precipitation of elemental sulphur, which was subsequently filtered off. The filtrate was then left to stand at ordinary temperature, when crystals of the appropriate dithiobiuret (often mixed with elemental sulphur) began to separate. The reaction took generally 36 to 72 hours for completion and the product was collected thereafter. The crude product after being dried was washed with a little carbon disulphide, which removed the accompanying sulphur. It was crystallised from water, dilute ethanol, or rectified spirit, as was found convenient. The reaction was carried out with methyl-, dimethyl-, ethyl-, propyl-$^n$, butyl$^n$-, and benzyl- amines. In every case the related dithiobiuret was obtained. The results are summarised in Table I.

TABLE I

Isopersulphocyanic acid used = 10 g.

| Expt. No. | Amines used. | Product formed. | M.P. | Formula. | Found. | Calc. |
|---|---|---|---|---|---|---|
| 1. | Methylamine (20 c.c. of 33% aq. soln.) | 1-methyl-D*-(5.5g.) | 153° | $C_3H_7N_3S_2$ | C: 24.22% | 24.16% |
| | | | | | H: 4.82 | 4.69 |
| | | | | | N: 27.94 | 28.18 |
| | | | | | S: 42.88 | 42.95 |
| 2. | Ethylamine (30 c.c. of 33% aq. soln.) | 1-Ethyl-D** (1st crop 4 g.; 2nd crop 0.5 g., pale yellow crystals) | †178° | $C_4H_9N_3S_2$ | C: 30.06 | 29.44 |
| | | | | | H: 5.71 | 5.52 |
| | | | †129° | | N: 25.56 | 25.76 |
| | | | | | S: 39.52 | 39.26 |
| 3. | Ethylamine (20 c.c. of 33% aq. soln.) | Do. Major part | 129° | $C_4H_9N_3S_2$ | C: 29.32 | 29.44 |
| | | | | | H: 5.34 | 5.52 |
| | | | | | N: 25.28 | 25.76 |
| | | | | | S: 39.48 | 39.26 |
| 4. | Propyl$^n$amine (35 c.c. of 40% aq. soln.) | 1-Propyl$^n$-D* (3.5g.) | 121° | $C_5H_{11}N_3S_2$ | C: 34.32 | 33.89 |
| | | | | | H: 6.15 | 6.21 |
| | | | | | N: 23.56 | 23.72 |
| | | | | | S: 35.88 | 36.15 |
| 5. | Butyl$^n$amine (40 c.c. of 33% aq. soln.) | 1-Butyl$^n$-D (3.5g.) | 115° | $C_6H_{13}N_3S_2$ | C: 37.91 | 37.69 |
| | | | | | H: 6.89 | 6.80 |
| | | | | | N: 21.85 | 21.98 |
| | | | | | S: 33.79 | 33.50 |
| 6. | Benzylamine (15 g. in ethanol, 30 c.c.) | 1-Benzyl-D | .. | Precipitated on acidification as a sticky solid which could not be crystallised; but the product was identified (vide Table II). | | |
| 7. | Dimethylamine (25 c.c. of 40% aq. soln.) | 1-Dimethyl-D (5.0 g.) | 131° | $C_4H_9N_3S_2$ | C: 29.74 | 29.44 |
| | | | | | H: 5.48 | 5.52 |
| | | | | | N: 25.26 | 25.76 |
| | | | | | S: 39.56 | 39.26 |

* Hecht, *Ber.*, 1892, **25**, 753, 754.

** Hecht (*loc. cit.*) gives m.p. 175°.

† These were probably dimorphous forms. Both gave the same thiuret on oxidation (vide Table II).

*N.B.*—D denotes 2,4-dithiobiurets.

*Oxidation of 1-Alkyl-substituted 2, 4-Dithiobiurets to Formation of the Related Thiurets (5-Alkylamino- 3-imino-1, 2, 4-dithioazolidines).*—A small quantity (2-3 g.) of the dithiobiuret was dissolved in ethanol (10-20 c.c.) and iodine in aqueous potassium iodide solution was added gradually with stirring till the pale yellow colour of the reaction mixture persisted. During addition of iodine or on cooling, after excess of iodine had been added, crystals began to separate. The last trace of unchanged iodine was removed by adding a little of bisulphite solution. The product was collected and crystallised from hot water or ethanol. In every case, it was found to be the hydriodide of the base. The results are presented in Table II.

TABLE II

| Expt. No. | Dithiobiuret oxidised. | 5-Alkylamino-3-imino-1, 2, 4-dithioazolidine hydriodide formed. | M.P. | Formula. | Found. | Calc. |
|---|---|---|---|---|---|---|
| 1. | 1-Methyl- | 5-Methylamino- | 204° | $C_4H_6N_3IS_2$ | C: 13.14%<br>H: 2.44<br>N: 15.08<br>S: 22.92 | 13.09%<br>2.18<br>15.27<br>23.27 |
| 2. | 1-Ethyl- | 5-Ethylamino- | 144° | $C_5H_8N_3IS_2$ | C: 17.70<br>H: 3.14<br>N: 14.58<br>S: 22.38 | 16.60<br>2.76<br>14.53<br>22.14 |
| 3. | 1-Propyl$^n$- | 5-Propyl$^n$amino- | 131-32° | $C_6H_{10}N_3IS_2$ | C: 19.88<br>H: 3.47<br>N: 13.82<br>S: 21.48 | 19.80<br>3.30<br>13.86<br>21.12 |
| 4. | 1-Butyl$^n$- | 5-Butyl$^n$amino- | 121° | $C_6H_{12}N_3IS_2$ | C: 22.93<br>H: 3.82<br>N: 13.30<br>S: 20.12 | 22.71<br>3.78<br>13.24<br>20.18 |
| 5. | 1-Benzyl- | 5-Benzylamino- | 184-85° | $C_9H_{10}N_3IS_2$ | C: 31.72<br>H: 2.86<br>N: 12.16<br>S: 18.46 | 30.76<br>2.84<br>11.96<br>18.23 |
| 6. | 1-Dimethyl- | 5-Dimethylamino- | 194° | $C_4H_8N_3IS_2$ | C: 15.85<br>H: 3.18<br>N: 14.13<br>S: 22.45 | 16.60<br>2.76<br>14.53<br>22.14 |

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# Charge and Stability of Colloids. Part XXIII. Displacement of Hydrogen Ions from $Sb_2S_3$ Sol by Addition of Electrolytes in Presence and in Absence of Non-electrolytes

**B. P. Yadava and Mohammad Yaseen**

The electrometric titrations have been carried out with $Sb_2S_3$ sol and the consequent release of hydrogen ions has been studied during the course of coagulation by stepwise addition of uni-, bi-, and tri-valent electrolytes. A relation between the coagulating power of different electrolytes has been found by comparing the amount of $H^+$ released at a particular concentration. Similar observations have been made to study the behaviour of the electrolytes in presence of non-electrolytes (agar agar, gelatin, and starch). Sensitising and stabilising tendencies of the non-electrolytes at different concentrations have been studied. The observations reveal that coagulating power increases as valencies of the coagulating ions are increased, leading to the proposed mechanism of the electrolytic coagulation.

During coagulation of $As_2S_3$ sol in presence of $Ba^{2+}$ as coagulating ion, Whitney and Ober (*J. Amer. Chem. Soc.*, 1901, **23,** 842) observed that the latter was adsorbed and an equivalent amount of $H^+$ ions was released. This was believed to be the case of hydrolytic adsorption, but Rabinovitch (*Z. physikal. Chem.*, 1925, **116,** 97) showed it to be an exchange adsorption of $H^+$ ions for $Ba^{2+}$ ions in the outer portion of double layer. The hydrogen-ion concentration of the sol may be determined conductometrically (Rabinovitch *et al.*, *ibid.*, 1928, **131,** 313; *Kolloid Z.*, 1932, **60,** 268); but the method is of doubtful accuracy, specially in sol-electrolyte mixtures. Weiser and Gray (*J. Phys. Chem.*, 1932, **36,** 2796) adopted the potentiometric method of analysis with glass electrode and determined the change in $H^+$-ion concentration on the stepwise addition of the coagulator. The cations carried down during coagulation of $As_2S_3$ sol are not equivalent to the $H^+$ ions displaced. Adsorption of cations varies widely with sols, depending on the method of their preparation, ageing, and concentration.

Using an undialysed sol, Rabinovitch *et al.* (*Z. physikal. Chem.*, 1931, **A154,** 255; 1929, **A143,** 21) determined the $H^+$-ion concentration, before and after coagulation of $As_2S_3$ sol, and found it to be equal to 1/2 $Ba^{2+}$ ions adsorbed. Pauli and Semler (*Kolloid Z.*, 1924, **34,** 45)

worked on a dialysed sol and found the ratio between $H^+$ ions released and the adsorbed 1/2 $Ba^{2+}$ to be 4 : 1 instead of 1 : 1, as reported earlier. In some of the previous papers of this series (Yadava, this *Journal*, 1943, **20**, 116, 123, 219) the displacement of chlorine ions from colloidal solutions of chromium, iron, and aluminium hydroxides was studied and the observations revealed that the displacement of counter ions in impure sol was more than the amount of coagulating ions added. The present work has been undertaken to study the effect of varying concentrations of non-electrolytes on the release of $H^+$ ions from $Sb_2S_3$ sols, when coagulated by stepwise addition of electrolytes.

## EXPERIMENTAL

An approximately 1% solution of antimony potassium tartrate was added dropwise to water, saturated with $H_2S$, with constant stirring. The excess of $H_2S$ was removed by passing pure hydrogen through the sol. The sol was left for 24 hours, filtered, and stored in a coloured bottle. Electrolytes and non-electrolytes of A.R. grade were employed and the solutions were prepared with conductivity water. The *p*H of the system was measured correct to the second place of decimals by using Philip's *p*H-meter, type G.M. 4494/96. Firstly the *p*H of the pure sol was determined. In six stoppered vessels of 50 c.c. capacity, 10 c.c. of sol was taken in each; to these increasing volumes (0, 1, 2, 3, 4, and 5 c.c.) of 0.01*N*-KCl solution together with requisite volumes of water were added to make up a total volume of 20 c.c. After one hour, the *p*H of each of the mixtures was determined. The *p*H of the mixture of sol and water and 0 c.c. electrolyte indicated the dilution effect on the *p*H. Similar sets of observations were made when the sol was coagulated by 0.005*N*-$BaCl_2$ and 0.005*N*-$AlCl_3$ solutions. In presence of varying concentrations of non-electrolytes, viz., agar agar, gelatin, and starch, the sol was coagulated by stepwise addition of the electrolyte and the *p*H was observed.

TABLE I

10 c.c. sol + 0.01*N*-KCl solution + water. Total volume = 20 c.c.

$Sb_2S_3$ sol = 2.253 g./litre. *p*H of the sol = 4.05.

| Electrolyte added. | *p*H. | $(H^+)\times 10^5$ | | $(K^+)\times 10^5$ equiv. of electrolyte added. |
|---|---|---|---|---|
| | | In soln. | Displaced. | |
| 0.0 c.c. | 4.17 | 6.76 | 0.00 | 0.0 |
| 0.5 | 4.11 | 7.76 | 1.00 | 25.0 |
| 1.0 | 4.07 | 8.51 | 1.75 | 50.0 |
| 2.0 | 4.03 | 9.33 | 2.57 | 100.0 |
| 3.0 | 4.02 | 9.55 | 2.79 | 150.0 |
| 4.0 | 4.01 | 9.77 | 3.01 | 200.0 |
| 5.0 | 4.01 | 9.77 | 3.01 | 250.0 |

TABLE II

0.01*N*-KCl soln. + 10 c.c. sol + 0.1% non-electrolyte soln. + water.
Conc. of $Sb_2S_3$ sol and its *p*H and total volume are same as in Table I.

| Electrolyte added. | 1 c.c. | | 2 c.c. | | 3 c.c. | | 4 c.c. | | 5 c.c. | |
|---|---|---|---|---|---|---|---|---|---|---|
| | *p*H. | $(H^+)\times10^5$ displaced. | *p*H. | $(H^+)\times10^5$ displaced. | *p*H. | $(H^+)\times10^5$ displaced. | *p*H. | $(H^+)\times10^5$ displaced. | *p*H. | $(H^+)\times10^5$ displaced. |
| | | | | | Agar agar. | | | | | |
| 0.0c.c. | 4.17 | 0.00 | 4.17 | 0.00 | 4.17 | 0.00 | 4.17 | 0.00 | 4.17 | 0.00 |
| 1.0 | 4.08 | 1.56 | 4.09 | 1.37 | 4.11 | 1.00 | 4.12 | 0.82 | 4.13 | 0.65 |
| 2.0 | 4.05 | 2.15 | 4.05 | 2.15 | 4.08 | 1.56 | 4.10 | 1.18 | 4.11 | 1.00 |
| 3.0 | 4.03 | 2.57 | 4.04 | 2.36 | 4.07 | 1.75 | 4.08 | 1.56 | 4.10 | 1.18 |
| 4.0 | 4.02 | 2.79 | 4.03 | 2.57 | 4.06 | 1.95 | 4.08 | 1.56 | 4.09 | 1.37 |
| 5.0 | 4.02 | 2.79 | 4.03 | 2.57 | 4.05 | 2.15 | 4.07 | 1.75 | 4.08 | 1.56 |
| | | | | | Gelatin. | | | | | |
| 1.0 | 4.06 | 1.95 | 4.08 | 1.56 | 4.09 | 1.37 | 4.11 | 1.00 | 4.12 | 0.82 |
| 2.0 | 4.02 | 2.79 | 4.04 | 2.36 | 4.06 | 1.95 | 4.08 | 1.56 | 4.10 | 1.18 |
| 3.0 | 4.01 | 3.01 | 4.03 | 2.57 | 4.05 | 2.15 | 4.07 | 1.75 | 4.09 | 1.37 |
| 4.0 | 4.00 | 3.24 | 4.02 | 2.79 | 4.04 | 2.36 | 4.06 | 1.95 | 4.08 | 1.56 |
| 5.0 | 4.00 | 3.24 | 4.02 | 2.79 | 4.04 | 2.36 | 4.06 | 1.95 | 4.08 | 1.56 |
| | | | | | Starch. | | | | | |
| 1.0 | 4.06 | 1.95 | 4.07 | 1.75 | 4.08 | 1.56 | 4.10 | 1.18 | 4.11 | 1.00 |
| 2.0 | 4.02 | 2.79 | 4.03 | 2.57 | 4.05 | 2.15 | 4.07 | 1.75 | 4.08 | 1.56 |
| 3.0 | 4.00 | 3.24 | 4.01 | 3.01 | 4.04 | 2.36 | 4.06 | 1.95 | 4.07 | 1.75 |
| 4.0 | 4.00 | 3.24 | 4.00 | 3.24 | 4.03 | 2.57 | 4.05 | 2.15 | 4.07 | 1.75 |
| 5.0 | 3.99 | 3.47 | 4.00 | 3.24 | 4.03 | 2.57 | 4.05 | 2.15 | 4.06 | 1.95 |

TABLE III

0.005*N*-$BaCl_2$ soln. + 10 c.c. sol + water. Total volume = 20 c.c.
$Sb_2S_3$ sol = 2.261 g./litre. *p*H of the sol = 4.07.

| Electrolyte added. | *p*H. | $(H^+)\times10^5$ | | $\frac{1}{2}(Ba^{++})\times10^5$ equiv. of electrolyte added. |
|---|---|---|---|---|
| | | In soln. | Displaced. | |
| 0.0 c.c. | 4.19 | 6.46 | 0.00 | 0.0 |
| 0.5 | 4.06 | 8.71 | 2.25 | 12.5 |
| 1.0 | 4.02 | 9.55 | 3.09 | 25.0 |
| 2.0 | 3.98 | 10.47 | 4.01 | 50.0 |
| 3.0 | 3.97 | 10.72 | 4.26 | 75.0 |
| 4.0 | 3.96 | 10.96 | 4.50 | 100.0 |
| 5.0 | 3.96 | 10.96 | 4.50 | 125.0 |

TABLE IV

0.005*N*-$BaCl_2$ soln. + 10 c.c. sol + 0.1% non-electrolyte soln. + water.
Conc. of $Sb_2S_3$ sol, *p*H and total volume are same as in Table III.

| Electrolyte added. | 1 c.c. *p*H. | 1 c.c. $(H^+) \times 10^5$ displaced. | 2 c.c. *p*H. | 2 c.c. $(H^+) \times 10^5$ displaced. | 3 c.c. *p*H. | 3 c.c. $(H^+) \times 10^5$ displaced. | 4 c.c. *p*H. | 4 c.c. $(H^+) \times 10^5$ displaced. | 5 c.c. *p*H. | 5 c.c. $(H^+) \times 10^5$ displaced. |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Agar agar. | | | | | | |
| 0.0c.c. | 4.19 | 0.00 | 4.19 | 0.00 | 4.19 | 0.00 | 4.19 | 0.00 | 4.19 | 0.00 |
| 1.0 | 4.03 | 2.88 | 4.04 | 2.66 | 4.05 | 2.46 | 4.07 | 2.05 | 4.09 | 1.67 |
| 2.0 | 3.99 | 3.77 | 4.00 | 3.54 | 4.02 | 3.09 | 4.04 | 2.66 | 4.06 | 2.25 |
| 3.0 | 3.98 | 4.01 | 3.99 | 3.77 | 4.01 | 3.31 | 4.03 | 2.88 | 4.05 | 2.46 |
| 4.0 | 3.97 | 4.26 | 3.98 | 4.01 | 4.01 | 3.31 | 4.03 | 2.88 | 4.04 | 2.66 |
| 5.0 | 3.97 | 4.26 | 3.98 | 4.01 | 4.00 | 3.54 | 4.02 | 3.09 | 4.04 | 2.66 |
| | | | | Gelatin. | | | | | | |
| 1.0 | 4.01 | 3.31 | 4.03 | 2.88 | 4.05 | 2.46 | 4.06 | 2.25 | 4.08 | 1.86 |
| 2.0 | 3.97 | 4.26 | 3.99 | 3.77 | 4.01 | 3.31 | 4.03 | 2.88 | 4.05 | 2.46 |
| 3.0 | 3.96 | 4.50 | 3.98 | 4.01 | 4.00 | 3.54 | 4.02 | 3.09 | 4.04 | 2.66 |
| 4.0 | 3.95 | 4.76 | 3.98 | 4.01 | 3.99 | 3.77 | 4.01 | 3.31 | 4.03 | 2.88 |
| 5.0 | 3.95 | 4.76 | 3.97 | 4.26 | 3.99 | 3.77 | 4.01 | 3.31 | 4.03 | 2.88 |
| | | | | Starch. | | | | | | |
| 1.0 | 3.99 | 3.77 | 4.01 | 3.31 | 4.04 | 2.66 | 4.06 | 2.25 | 4.08 | 1.86 |
| 2.0 | 3.96 | 4.50 | 3.97 | 4.26 | 4.00 | 3.54 | 4.03 | 2.88 | 4.05 | 2.46 |
| 3.0 | 3.95 | 4.76 | 3.96 | 4.50 | 3.98 | 4.01 | 4.01 | 3.31 | 4.03 | 2.88 |
| 4.0 | 3.95 | 4.76 | 3.96 | 4.50 | 3.97 | 4.26 | 4.01 | 3.31 | 4.02 | 3.09 |
| 5.0 | 3.95 | 4.76 | 3.95 | 4.76 | 3.97 | 4.26 | 4.00 | 3.54 | 4.02 | 3.09 |

TABLE V

0.005*N*-$AlCl_3$ soln. + 10 c.c. sol + water. Total volume = 20 c.c.
$Sb_2S_3$ sol = 2.25 g./litre. *p*H of the sol = 4.04.

| Electrolyte added. | *p*H. | $(H^+) \times 10^5$ In soln. | $(H^+) \times 10^5$ Displaced. | $\frac{1}{3}(Al)^{3+} \times 10^5$ equiv. of electrolyte added. |
|---|---|---|---|---|
| 0.0 c.c. | 4.16 | 6.92 | 0.00 | 0.0 |
| 0.5 | 4.01 | 9.77 | 2.85 | 12.5 |
| 1.0 | 3.97 | 10.72 | 3.80 | 25.0 |
| 2.0 | 3.94 | 11.48 | 4.56 | 50.0 |
| 3.0 | 3.93 | 11.75 | 4.83 | 75.0 |
| 4.0 | 3.93 | 11.75 | 4.83 | 100.0 |
| 5.0 | 3.93 | 11.75 | 4.83 | 125.0 |

TABLE VI

0.005*N*-$AlCl_3$ soln. + 10 c.c. sol + 0.1% non-electrolyte soln. + water.
Conc. of $Sb_2S_3$ sol, its *p*H and total volume are same as in Table V.

| Electrolyte added. | 1 c.c. | | 2 c.c. | | 3 c.c. | | 4 c.c. | | 5 c.c. | |
|---|---|---|---|---|---|---|---|---|---|---|
| | *p*H. | $(H^+) \times 10^5$ displaced. | *p*H. | $(H^+) \times 10^5$ displaced. | *p*H. | $(H^+) \times 10^5$ displaced. | *p*H. | $(H^+) \times 10^5$ displaced. | *p*H. | $(H^+) \times 10^5$ displaced. |
| | | | | | Agar agar. | | | | | |
| 0.0c.c. | 4.16 | 0.00 | 4.16 | 0.00 | 4.16 | 0.00 | 4.16 | 0.00 | 4.16 | 0.00 |
| 1.0 | 3.99 | 3.31 | 4.01 | 2.85 | 4.04 | 2.20 | 4.05 | 1.99 | 4.06 | 1.79 |
| 2.0 | 3.96 | 4.04 | 3.98 | 3.55 | 4.00 | 3.08 | 4.02 | 2.63 | 4.03 | 2.42 |
| 3.0 | 3.95 | 4.30 | 3.97 | 3.80 | 3.99 | 3.31 | 4.00 | 3.08 | 4.02 | 2.63 |
| 4.0 | 3.94 | 4.56 | 3.96 | 4.04 | 3.99 | 3.31 | 4.00 | 3.08 | 4.01 | 2.85 |
| 5.0 | 3.94 | 4.56 | 3.95 | 4.30 | 3.98 | 3.55 | 3.99 | 3.31 | 4.01 | 2.85 |
| | | | | | Gelatin. | | | | | |
| 1.0 | 3.95 | 4.03 | 3.99 | 3.31 | 4.03 | 2.41 | 4.05 | 1.99 | 4.06 | 1.79 |
| 2.0 | 3.93 | 4.83 | 3.96 | 4.04 | 3.99 | 3.31 | 4.01 | 2.85 | 4.02 | 2.63 |
| 3.0 | 3.93 | 4.83 | 3.95 | 4.30 | 3.97 | 3.80 | 3.99 | 3.31 | 4.01 | 2.85 |
| 4.0 | 3.93 | 4.83 | 3.94 | 4.56 | 3.95 | 4.04 | 3.98 | 3.55 | 4.00 | 3.08 |
| 5.0 | 3.92 | 5.10 | 3.94 | 4.56 | 3.95 | 4.30 | 3.98 | 3.55 | 4.00 | 3.08 |
| | | | | | Starch. | | | | | |
| 1.0 | 3.94 | 4.56 | 3.96 | 4.04 | 4.00 | 3.08 | 4.03 | 2.41 | 4.04 | 2.20 |
| 2.0 | 3.93 | 4.03 | 3.94 | 4.56 | 3.97 | 3.80 | 3.99 | 3.31 | 4.01 | 2.85 |
| 3.0 | 3.92 | 5.10 | 3.93 | 4.83 | 3.96 | 4.04 | 3.98 | 3.55 | 3.99 | 3.31 |
| 4.0 | 3.92 | 5.10 | 3.93 | 4.83 | 3.96 | 4.04 | 3.97 | 3.80 | 3.98 | 3.55 |
| 5.0 | 3.92 | 5.10 | 3.92 | 5.10 | 3.95 | 4.30 | 3.97 | 3.80 | 3.98 | 3.55 |

## DISCUSSION

The displacement of hydrogen ions from $Sb_2S_3$ sol by ions of different valency shows a remarkable similarity in the coagulating power of these ions corresponding to their valency, e.g., a certain concentration of $Al^{3+}$ ions releases more $H^+$ ions than the same amount of $Ba^{2+}$ ions does. Being a monovalent ion, potassium has lesser effect on the release of counter ions as compared to $Ba^{2+}$ and $Al^{3+}$ ions. The equivalent amount of coagulating ion has been calculated in each set of observations and it is found (Table I) that in the case of potassium as coagulating ion, the ratio between $H^+$ ion released and the equivalent amount of $K^+$ used is 1 : 25, in the early stages of coagulation, whereas when $Ba^{2+}$ and $Al^{3+}$ are used as coagulating ions, this ratio becomes approximately 1 : 6 and 1 : 4 respectively (Tables III and V).

While studying the effect of non-electrolytes on the displacement of $H^+$ ions, it was observed that small, amounts (*i.e.*, 1 c.c.) of gelatin and starch sensitised the sol while agar agar protected it at all concentrations. At higher concentrations (above 2 c.c.) all these non-electrolytes show a protective action towards coagulation of the $Sb_2S_3$ sol. In the case of potassium as coagulating ion, a ratio of 1 : 25 is obtained between hydrogen ions released and potassium ions used, but in the presence of 5 c.c. of 0.1% agar agar solution this ratio is 1 : 80 and in presence of the same amount of gelatin and starch, this ratio is 1 : 60 and 1 : 50 respectively (Table II). Similar observations in the case of Ba and Al salts show that the protective action of the non-electrolytes decreases in the following order : K, Ba, Al (Tables II, IV, and VI). These observations give us a comparative idea of the coagulating power of different ions and the protective effect of different non-electrolytes to suppress the coagulation of colloids in their presence.

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# Studies on the Fries Rearrangement. Part II*

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The reaction temperature, nature and amount of the catalyst, nature of the solvent, and nature and size of the acy group have been studied in the Fries transposition.

In continuation of our work (this *Journal*, 1958, **35,** 881) on the course of the Fries rearrangement, we have investigated the rearangement of 2-bromo-4-methylphenyl acetate, phenyl-β-cyclohexyl propionate, and phenyl-γ-cyclohexyl butyrate under the following conditions:

(*a*). (*i*) At 100° in presence of a solvent, and (*ii*) at 110° without a solvent, using anhydrous aluminium chloride, zinc chloride, stannic chloride, ferric chloride, and boron trifluoride as catalysts.

(*b*). With aluminium chloride (*i*) at 110° in different molecular proportions, and (*ii*) at different temperatures.

At 100° in nitrobenzene and at 110° without solvent, the phenyl-β-cyclohexyl propionate and phenyl-γ-cyclohexyl butyrate gave mainly *p*-hydroxy ketones. In the case of the former 13% of *o*-hydroxy and 51% of *p*-hydroxy ketones were obtained when $CS_2$ was used as a solvent, but at 140°, it furnished 60% of the *ortho* isomer and none of the *para* isomer (Table IV).

Effect of the proportion of the catalyst was studied using 0.25, 0.5, 1.0, 1.5, 3.0, and 4.0 moles of anhydrous aluminium chloride on the above esters. In all cases the reaction was carried out at 110°, without any solvent, for 2 hours. The rearrangement was found best when 3 moles of the catalyst were used (Table III). Benzene was found to act as a better solvent than nitrobenzene, toluene or $CS_2$ (Table IV). Regarding the catalysts, aluminium chloride was found to be the best (Table I).

*Part I: This *Journal*, 1958, **35,** 881.

At low temperature cyclohexanepropionyl and cyclohexanebutyryl groups migrated to *para* position, but at higher temperatures, migration to *ortho* position took place (Table II).

## EXPERIMENTAL

*2-Bromo-4-methylphenyl acetate* was prepared as usual (Tiwari and Singh, *loc. cit.*) from 2-bromo-4-methylphenol (20 g.) and acetyl chloride (10 g.); b.p. 120°/3mm, yield 60%. (Found : C, 47.12 ; H, 3.92. $C_9H_9O_2Br$ requires C, 47.16 ; H, 3.93%).

*Phenyl-β-cyclohexyl propionate and phenyl-γ-cyclohexyl butyrate* were prepared as usual (Tiwari and Singh, this *Journal*, 1959, **36,** 496 ; *loc. cit.*).

### *Rearrangement in Presence of Solvent*

*Nitrobenzene.*—The reaction was carried out in the usual manner by taking aluminium chloride (anhyd., 1.5 *M*), freshly distilled nitrobenzene (15 c.c.), and esters (1 *M*). The mixture was refluxed on a water bath for 2 hours. *o*-Hydroxy ketones and nitrobenzene were separated from the mixture by steam distillation and subsequently the ketones were isolated and characterised in the usual way (Tiwari and Tripathi, *ibid.*, 1954, **31,** 841). The residue left after steam distillation was worked up for *p*-hydroxy ketones.

*Benzene.*—The ester (1 *M*) was suspended in benzene (15 c.c.) and anhydrous aluminium chloride (1.5 *M*) was added to it. The reaction was carried out on a water bath for 2 hours and was worked up for the isolation and characterisation of hydroxy ketones in the usual way (Tiwari and Singh, *loc. cit.*) (Table IV).

*Toluene & Carbon Disulphide.*—The rearrangements in toluene and in $CS_2$ were studied as in the case of benzene.

### *Rearrangement in Absence of Solvent*

Fries rearrangement of the esters were carried out with anhydrous aluminium chloride, zinc chloride, stannic chloride, and ferric chloride as catalysts (1.5 *M*) in the usual way. In the case of boron trifluoride as catalyst, the temperature was maintained at 100°, and after decomposition with HCl (dil.) and ice, the product was steam distilled ; the *o*-hydroxy ketone from the distillate and the *p*-hydroxy ketone from the residue were isolated and characterised in the usual way (Karl *et al.*, *Chem. Ber.*, 1954, **87,** 194 ; Tiwari and Singh, *loc. cit.*) (vide Table I).

TABLE I

*Effect of different catalysts in nitrobenzene.*

Ester taken = 2 g. Heated at 100° for 2 hrs.

| No. | Ester. | Ketone. | $AlCl_3$. | $ZnCl_2$. | $SnCl_4$. | $FeCl_3$. | $BF_3$. |
|---|---|---|---|---|---|---|---|
| 1. | 2-Bromo-4-methylphenyl acetate | *o*-Hydroxy | 1.8 g. | 1.7 g. | 1.4 g. | 1.1 g. | 1.6 g. |
| | Phenyl-β-cyclohexyl propionate | *p*- „ | 1.4 | 1.3 | 1.0 | 0.3 | 1.0 |
| 3. | Phenyl-γ-cyclohexyl butytate | *p*- „ | 1.5 | 1.3 | 1.1 | 0.5 | 0.7 |

*Effect of the Proportion of the Catalyst*

Rearrangement of 2-bromo-4-methylphenyl acetate, phenyl-β-cyclohexyl propionate, and phenyl-γ-cyclohexyl butyrate was carried out at 110° without solvent, using 0.25, 0.5, 1.0, 1.5, 3.0, and 4.0 moles of anhydrous aluminium chloride for 2 hours as usual.

TABLE II

Ester taken = 2 g.

| * Ester. | Ketone. | Amount of anhydrous aluminium chloride (in *M*). 0.25 | 0.5. | 1.0. | 1.5. | 3.0. | 4.0. |
|---|---|---|---|---|---|---|---|
| 1. | *o*-Hydroxy | Nil | Nil | Traces | 1.8 g. | 1.9 g. | 1.5 |
| 2. | *p*- ,, | Nil | Nil | Nil | 1.0 | 1.3 | 1.2 |
| | *o*- ,, | X | X | X | Traces | X | X |
| 3. | *p*- ,, | Nil | Nil | Nil | 1.2 | 1.5 | 1.2 |

* The number corresponds to those in Table I.

*Effect of Temperature*

The effect of temperature was studied in the case of the three esters without solvent and keeping temperature at 100°, 110°, 120°, and 140° for 2 hours as usual.

TABLE III

Ester taken = 2 g. $AlCl_3$ = 1.5 *M*.

| * Ester. | Ketone. | 100°. | 110°. | 120°. | 140°. |
|---|---|---|---|---|---|
| 1. | *o*-Hydroxy | Traces | 1.8 g. | 1.7 g. | 1.4 g. |
| 2. | *o*- ,, | X | X | 0.9 | 1.2 |
| | *p*- ,, | X | 1.0 | Traces | X |
| 3. | *o*- ,, | X | X | 0.5 | 1.1 |
| | *p*- ,, | X | 1.2 | X | X |

* Same as in Table I.

*Effect of Solvent*

The rearrangement of the esters was carried out in the different solvents, viz., nitrobenzene, $CS_2$, benzene, and toluene on a steam bath.

TABLE IV

Ester taken = 2 g. $AlCl_3$ = 1.5 *M*.

| * Ester. | Ketone. | $C_6H_5NO_2$. | $CS_2$. | $C_6H_6$. | $C_7H_8$. |
|---|---|---|---|---|---|
| 1. | *o*-Hydroxy | 1.8 g. | 1.8 g. | 1.9 g. | 1.2 g. |
| 2. | *o*- ,, | .. | 0.3 | .. | .. |
| | *p*- ,, | 1.4 | 1.0 | 1.3 | 0.9 |
| 3. | *p*- ,, | 1.5 | 1.3 | 1.3 | 0.8 |

* Same as in Table I.

TABLE V

| | o-Hydroxy ketones. | | | | | | | 2:4-Dinitrophenylhydrazone. | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| * Ester. | B. P. | Yield. | Formula. | % Carbon. Found. | Calc. | %Hydrogen. Found. | Calc. | M.P. | Formula. | %Nitrogen. Found. | Calc. |
| 1. | 126-27°/2mm | 89% | $C_8H_9O_2Br$ | 47.11 | 47.16 | 3.92 | 3.93 | 258° | $C_{14}H_{13}O_5N_4Br$ | 13.68 | 13.69 |
| 3. | 220°/5 | 55 | $C_{16}H_{22}O_2$ | 78.10 | 78.17 | 8.92 | 8.95 | 125° | $C_{22}H_{26}O_5N_4$ | 13.15 | 13.15. |

* Number same as in Table1

The physical data of phenyl-γ-cyclohexyl butyrate and *o*-and *p*-hydroxy ketones derived from phenyl-βcyclohexyl propionate have been recorded in previous papers (*loc. cit.*).

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# SHORT NOTES

## Effect of Alkali on the Reduction of Potassium Permanganate by Selenium Dioxide

**Kundan Lal and Mohinder Singh Sohal**

In the earlier publications (Lal *et al.*, this *Journal*, 1959, **36,** 167 ; *J. Sci. Ind. Res.*, 1960, **19B,** 162) it has been reported that reduction of permanganates by selenium dioxide, in the acidic medium, yields selenic acid, the metal selenate, manganous selenite, manganic diselenite, manganese selenate (only traces), and a complex compound, $xR_2O$. $yMnO$. $zMnO_2$. The present work has been undertaken with a view to studying the effect of alkali on various reaction products.

*Procedure.*—To a 1% $KMnO_4$ solution (50 c.c.), made alkaline with 4, 6, 8, 10, and 12 c.c. of *N*-KOH solution respectively, a 5% aqueous solution of selenium dioxide was dropped slowly to just discharge the pink colour. The filtrates and precipitates were analysed completely.

The medium of reaction, which became finally alkaline, passed through acidic and neutral stages. The analytical results of the end products show that almost similar products are formed in the acidic and the neutral media while in the alkaline medium these differ considerably (Table I). The results obtained in the alkaline medium have further been verified by studying all the three stages of reduction of potassium permanganate by potassium selenite (Table II).

It appears that selenic acid, produced in the reaction, is neutralised by the free alkali with the result that as the volume of *N*-KOH added increases, the amount of acid decreases, and potassium selenate content subsequently increases. Existence of potassium oxide, which is noticed even in the acidic medium, is probably due to the reason that this is firmly held by the hydrated manganese dioxide, possessing feebly acidic properties. Formation of manganese selenate in the acidic and neutral media may be regarded to be produced as a result of direct interaction of the freshly precipitated hydrated manganese dioxide and selenium dioxide. In the coloured stage, manganese selenate is, however, acted upon by the unused permanganate, and therefore it disappears completely. In the alkaline medium, the absence may be due to its reaction with free alkali. Both manganous selenite and manganic diselenite are most probably acted upon by the free alkali and the resulting potassium selenite is further oxidised by the oxygen liberated by the mutual interaction of permanganate and free alkali, as suggested by Sackur and Taegener (*Z. Elektrochem.*, 1912, **18,** 718).

TABLE I

*Analyses of reaction mixtures obtained when alkaline* 1% $KMnO_4$ (50 *c.c.*) *solution is just decolorised with* 5% $SeO_2$ *solution.*

| No. | *N*-KOH added | $SeO_2$ soln. required. | Medium. | Filtrate. $K_2SeO_4$. | Filtrate. KOH. | Precipitate. $H_2SeO_4$. | Precipitate. $MnSeO_3$. | Precipitate. $MnSe_2O_6$. | Precipitate. $K_2O$. | Precipitate. MnO. | Precipitate. $MnO_2$. | Approx. mol. ratio. $K_2O$: MnO: $MnO_2$. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. | 4.00c.c. | 13.70c.c. | | 0.7367g. | | 0.2393g. | 0.0399g. | 0.0358g. | 0.0241g. | 0.0429g. | 0.1945g. | 1:2:9 |
| | 4.00 | 13.70 | Acidic | 0.7352 | Nil | 0.2393 | 0.0396 | 0.0361 | 0.0229 | 0.0427 | 0.1942 | 1:2:9 |
| 2. | 6.00 | 13.80 | | 0.9630 | | 0.1187 | 0.0331 | 0.0266 | 0.0237 | 0.0474 | 0.1931 | 1:3:9 |
| | 6.00 | 13.80 | ,, | 0.9597 | ,, | 0.1179 | 0.0333 | 0.0261 | 0.0223 | 0.0469 | 0.1928 | 1:3:9 |
| 3. | 8.00 | 13.70 | | 1.1599 | | 0.0 | 0.0254 | 0.0164 | 0.0304 | 0.0510 | 0.1935 | 1:2:7 |
| | 8.00 | 13.70 | Neutral | 1.1632 | ,, | Nil | 0.0248 | 0.0160 | 0.0300 | 0.0520 | 0.1931 | 1:2:7 |
| 4. | 10.00 | 13.20 | | 1.1768 | 0.0740 | | | | 0.0584 | 0.0732 | 0.1850 | 1:2:3 |
| | 10.00 | 13.20 | Alkaline | 1.1749 | 0.0759 | Nil | Nil | Nil | 0.0588 | 0.0728 | 0.1844 | 1:2:3 |
| 5. | 12.00 | 13.10 | ,, | 1.1782 | 0.1848 | | | | 0.0585 | 0.0740 | 0.1846 | 1:2:3 |
| | 12.00 | 13.15 | ,, | 1.1756 | 0.1872 | Nil | Nil | Nil | 0.0582 | 0.0736 | 0.1842 | 1:2:3 |

TABLE II

*Analyses of reaction mixtures obtained in the reduction of* 1% $KMnO_4$ (50 *c.c.*). *solution by* 5% $K_2SeO_3$ *solution (aq.).*

| No. | $K_2SeO_3$ soln. added | Stage of reaction. | Filtrate. $KMnO_4$ decomp. | Filtrate. $K_2SeO_4$. | Filtrate. KOH. | Precipitate. $K_2SeO_3$ unused. | Precipitate. $K_2O$. | Precipitate. MnO. (g.) | Precipitate. $MnO_2$. (g.) | Approx. mol. ratio. $K_2O$: MnO: $MnO_2$. |
|---|---|---|---|---|---|---|---|---|---|---|
| *1. | 9.60c.c. | | 54.92% | 0.5237g. | 0.0511g. | | 0.0330 | 0.0458 | 0.0940 | 1:2:3 |
| | 9.60 | Coloured | 54.92 | 0.5315 | 0.0511 | Nil | 0.0332 | 0.0458 | 0.0943 | 1:2:3 |
| *2. | 14.40 | | 80.00 | 0.7782 | 0.0911 | | 0.0426 | 0.0667 | 0.1368 | 1:2:3 |
| | 14.00 | | 80.00 | 0.7775 | 0.0911 | ,, | 0.0424 | 0.0663 | 0.1362 | 1:2:3 |
| 3. | 19.20 | | 100.00 | 1.0410 | 0.1122 | | 0.0543 | 0.0834 | 0.1708 | 1:2:3 |
| | 19.20 | Intermediate | 100.00 | 1.0398 | 0.1122 | ,, | 0.0544 | 0.0839 | 0.1711 | 1:2:3 |
| 4. | 21.70 | | 100.00 | 1.0434 | 0.1172 | 0.1232g. | 0.0545 | 0.0848 | 0.1701 | 1:2:3 |
| | 21.70 | Colorless | 100.00 | 1.0440 | 0.1155 | 0.1209 | 0.0546 | 0.0852 | 0.1708 | 1:2:3 |
| 5. | 24.20 | | 100.00 | 1.0420 | 0.1206 | 0.2484 | 0.0544 | 0.0836 | 0.1704 | 1:2:3 |
| | 24.20 | | 100.00 | 1.0427 | 0.1206 | 0.2462 | 0.0545 | 0.0836 | 0.1711 | 1:2:3 |

* The reaction mixtures were filtered after an interval of about 24 hours.

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# Synthesis of Nitrophenacyl Bromides

H. G. Garg*

Phenacyl bromide and its substituted analogues have been used for the synthesis of 2,5-diphenylpyrazines (Staedel and Rugheimer, *Ber.*, 1876, **9,** 563; Wolff, *Ber.*, 1887, **20,** 432; Gabriel, *Ber.*, 1908, **41,** 1131; Tutin, *J. Chem. Soc.*, 1919, **97,** 2500; Ochai *et al.*, *J. Pharm. Soc., Japan,* 1939, **59,** 462) and aroylbenzofurans (Rap, *Gazzetta,* 1895, **25,** 285; Sen and Saxena, this *Journal*, 1958, **35,** 136; 1959, **36,** 283).

In connection with the preparation of some nitro derivatives of pyrazines and aroylbenzofurans, required for some investigations, a few nitrophenacyl bromides, namely, 3-nitro-4-chloro-, 3-nitro-4-bromo-, 3-nitro-4-methyl-, 2, 4-dichloro-5-nitro- and 3, 4-dichloro-5-nitro-phenacyl bromides have been obtained. When acidified ethanolic solution of potassium iodide is allowed to react and warmed, iodine is set free. On titrating against a standard sodium thiosulphate solution, it has been found that in all cases liberation of iodine is nearly quantitative and original acetophenone is obtained (cf. Garg *et al.*, *Agra Univ. J. Res.*, 1957, **6,** 19; this *Journal*, 1957, **34,** 286).

4-Chloro-, 4-bromo-, and 4-methyl- acetophenones were obtained by Friedel-Crafts' acetylation of the corresponding substituted benzenes. 2,4-Dichloro- and 3, 4-dichloro-acetophenones were synthesised from the respective dichlorobenzenes, following the method described by Sodhan, Kshatriya, and Nargund (this *Journal*, 1947, **24,** 373). 3-Nitro-4-chloro- (Le Fevre and Le Fevre, *J. Chem. Soc.*, 1932, 1991; Kenford and Simpson, *ibid.*, 1947, 227), 3-nitro-4-bromo-(Ganguly and Le Fevre, *ibid.*, 1934, 852), 3-nitro-4-methyl-(Errera, *Gazzetta,* 1891, **21,** 92), 3, 4-dichloro-5-nitro-(Roberts and Tuner, *J. Chem. Soc.*, 1927, 1832), 2, 4-dichloro-5-nitro-(Sacha and Patel, this *Journal*, 1957, **34,** 821) acetophenones were prepared by nitration of the corresponding acetophenones.

*3-Nitro-4-chlorophenacyl Bromide.*—3-Nitro-4-chloroacetophenone (0.5*M*), dissolved in glacial acetic acid (300 g.), was warmed and treated with bromine (0.5*M*) dropwise. Acetic acid was distilled off and the phenacyl bromide was purified by recrystallisation from ethanol. Its characteristics and analytical data are shown in Table I.

By adopting this method, different colorless phenacyl bromides were prepared; their characteristics are shown in Table I.

TABLE I

| No. | Phenacyl bromide. | Yield. | M.P. | Formula. | % Halogen. Found. | Calc. |
|---|---|---|---|---|---|---|
| 1. | 3-Nitro-4-chloro- | 81% | 84° | $C_8H_5O_3NBrCl$ | 41.30 | 41.37 |
| 2. | 3-Nitro-4-bromo- | 78 | 94° | $C_8H_5O_3NBr_2$ | 49.21 | 49.53 |
| 3. | 3-Nitro-4-methyl- | 81 | 58° | $C_9H_8O_3NBr$ | 30.92 | 31.00 |
| 4. | 2,4-Dichloro-5-nitro- | 74 | 76° | $C_8H_4O_3NBrCl_2$ | 47.88 | 48.24 |
| 5. | 3,4-Dichloro-5-nitro- | 78 | 138° | $C_8H_4O_3NBrCl_2$ | 47.98 | 48.24 |

Author's sincere thanks are due to Dr. S. S. Joshi, Director, School of Chemistry and Principal, Meerut College, for his interest and to the Ministry of Scientific Research and Cultural Affairs, Government of India, for a research scholarship.

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| Sulphate ($SO_4$) | 0.01 | 0.005 | 0.01 |
| Aluminium (Al) | 0.003 | .. | .. |
| Calcium (Ca) | 0.005 | .. | .. |
| Chloride and Bromide (Cal) | .. | 0.025 | .. |
| Iodate ($IO_3$) | .. | 0.0002 | .. |
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| Iron (Fe) | .. | 0.001 | 0.001 |
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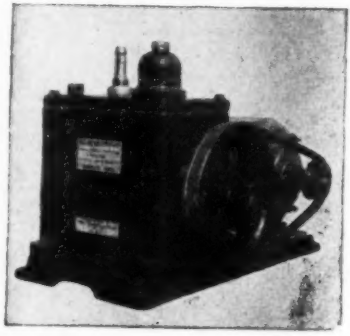

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